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Radiation induced polymerization of methyl methacrylate

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RADIATION INDUCED POLYMERIZATION OF METHYL METHACRYLATE

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ABSTRACT

A study has been made of the gamma radiation effect on the rate of polymerization of methyl methacrylate monomer, and also to determine the effects of the presence of clay of known composition and of other solids on the rate of polymerization. The results indicate that the monomer undergoes polymerization and then degradation as a function of radiation time at a given gamma flux.

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I. INTRODUCTION

The knowledge that x-ray, gamma and neutron radiation was capable of inducing polymerization of some simple monomer units began to develop in the late 1930's. Studies on some polymers by electron diffraction indicated that electron bombardment produced changes in their physical properties. However, a major limitation arose from the limited power output or penetration of the radiation sources available at the time. In the last two decades, the adequate sources of radiation have become readily available and there has been a rapidly increasing interest in the effect of radiation on a variety of materials. At the same time, the study of polymers has been recognized as a distinct branch of science with close connections with certain branches of organic chemistry, solid state physics, and physical chemistry. These favorable conditions have encouraged a rapid development of the earlier discoveries.

The effect of radiation on polymers may be considered from two aspects; certain of the permanent changes produced can be deleterious while others may be beneficial in character. Both aspects have one basic factor in common; the need to study the mechanism by which radiation affects polymers and to find ways by which these reactions can be controlled.

The purpose of this investigation was to ascertain the effects of gamma radiation on polymerization rate of methyl methacrylate monomer. A second aspect was to determine the rate of conversion of monomer to polymer in the presence of clay and other solids.

II. LITERATURE REVIEW

Nuclear reactors[1] which yield considerable amounts of radiation can be utilized directly for conversion of monomers to polymers. Most nuclear reactors contain uranium as the fissionable material and a moderator to slow down the fast neutrons to thermal velocities. Specimens placed within them are subjected to a mixture of radiations; primarily fast and slow neutrons and gamma radiation. The fission products, if long lived, can be separated to give sources of higher purity with a well-defined type of radiation.

The units of radiation[2] normally employed can be described in these ways: (a) units of radioactivity which express the rate at which the nuclei of radioactive elements disintegrate; (b) units of radiation intensity or flux which express the rate of emission or absorption of energy, where the rate of absorption is often called the dose rate and (c) units of integrated intensity, or dose, in which the absorbed radiation flux is integrated over the period of irradiation.

The commonly employed units of radio-activity and dose are summarized in Table 1.

TABLE 1.

Units of High Energy Radiation[3]

1 curie	The quantity of radio-active material giving 3.700×10^{10} disintegrations per second.
W	The energy required to form one ion pair in air. This is 32.5 e.v.* for γ-rays & about 35 e.v. for heavy particles.
1 roentgen, r	Produce 1 e.s.u. of charge in 1 cm^3 (0.0001293g) of air at $0^{\circ}C$. & 760 mm. . or 2.1×10^9 ion pairs. Equivalent to absorption of 83 ergs per g. of air, or about 93 ergs per g. of water and many organic molecules.
1 roentgen equivalent physical, rep	The quantity of radiation of any kind producing 83 ergs/g. of body tissue or water.
1 rad.	The quantity of radiation of any kind producing 100 ergs/g. of the absorber concerned.
1 rem	The quanitty of radiation of any kind producing biological damage in man equivalent to that caused by 1 r of x- or γ-radiation.
1 pile unit	Exposure to 10^{17} thermal neutrons per square centimeter, plus associated γ-rays and fast neutrons.
Megawatt per central ton (M.w.d./c.t.)	Equivalent to 3×10^{17} n.v.t.

* e.v. The electron volt is a unit corresponding to 1.60×10^{-12} ergs.

A number of possible mechanisms for the transfer of energy and for molecular dissociation in the gas phase have been proposed.[4] Lind[9] has defined the radiochemical yield as the quantity M/N, where M is the number of molecules produced or made to react per 100 e.v. of absorbed radiation. A cluster theory has been proposed by Lind[9] to explain the radiochemical reactions that the ions undergo. Eyring et. al.[10] have also studied the formation of excited molecules which is a general phenomenon occurring during the radiation process.

In solid and liquid phases several circumstances combine to reduce the number of possible reactions of ions and excited molecules so that the number of products formed is often relatively small and the over-all reaction appears relatively simple. These circumstances are as follows: (1) The deactivation of excited molecules in condensed systems will be more rapid because of the greater frequency of collisions. Excitation energy may be transferred from excited molecules to relatively stable ones, causing dissociation of the latter. A relatively stable solvent may thus promote the decomposition of a more sensitive solute. (2) In polar liquids, the effects of solvation may modify the stability of ions formed and their probability of being transformed into radicals. (3) Ion and radical recombinations will proceed readily in condensed

systems. (4) Immediate recombination of radicals may occur through the operation of the Franck-Rabinowitch "cage" mechanism.[11] The neighboring molecules may prevent radicals from diffusing away from each other, and therefore no net reaction or a greatly reduced frequency of dissociation will result.

It appeared to the pioneer investigators of radiation-initiated reactions that not only the ions but also the excited molecules were responsible in causing the chemical reactions.[9][10] Furthermore, the specific mechanism of reaction was believed to involve large ionic clusters. However, at the present time there seems to be general agreement that other reactions of ions are involved other than the formation of large ionic clusters.[13]

The cluster theory of radiation-initiated reaction was originally proposed by Lind.[9][12] According to the cluster theory, neutral molecules are attracted to an ion to form a cluster of molecules which can then share the charge of the original ion. Upon neutralization by an electron, the molecules in the cluster react chemically to yield products that are characteristic of the system being irradiated.

The present importance attached to the reactions of ions other than the clustering reaction, and the reactions of excited

molecules was reflected in a relatively recent symposium on the mechanism of radiation chemistry.[14] Lind,[15] in introducing the symposium, reviewed some of the experimental data which support the cluster theory. At the same time he recognized the theoretical evidence supporting the view that the chemical effects of radiationwere brought about by the action of free radicals or atoms.

TABLE 2

Summary of Reactions

	$N \rightarrow N^+ + \epsilon$	1
Radiation		
	$N \rightarrow N^*$	2
	$N^+ + \epsilon \rightarrow N^*$	3
Ions	$N^+ + (b-1)N \rightarrow [bN]^+$	4
	$[bN]^+ + \epsilon \rightarrow N_b^*$	5
	$N^* + N \rightarrow N + N$	6
Excited Molecules	$N^* \rightarrow \gamma R_1$	7
	$R_i + N \rightarrow R_{i+1}$	8
Free Radicals	$R_i + R_j \rightarrow M$	9

The summary of reactions given in Table 2 illustrates the general role of ions, excited molecules, and free radiculs in radiation-initiated reactions. Reactions 1 and 2 indicate the overall result of the physical processes that occur when a high-energy photon interacts with matter. Reaction 3 depicts the neutralization of an isolated ion by a thermal electron. The resulting excited molecule must have sufficient energy to allow rupture of the double bond in the monomer molecule. The cluster mechanism of Lind is indicated by reactions 4 and 5. In reaction 4, the positive charge of an ion is shared by a cluster consisting of a total of b monomer molecules. Upon neutralization by an electron, the clustered molecules react chemically to yield a product molecule containing an average of b monomer units, as indicated by reaction 5. Depending upon the specific mechanism of the reaction of the cluster, the product molecule may have either a free radical or excited nature.

Reactions 6 and 7 are characteristic of excited molecules. The excited molecules may arise either as a direct result of radiation absorption 2, or as the result of an ion neutralization process (3 and 5). In reaction 6, an excited molecule loses its energy in a series of molecular collisions if some other reaction does not occur before the de-excitation

process is complete. If properly excited, a molecule may decompose into free radicals as indicated by reaction 7[13].

Seitzer, Goeckermann, and Tobolsky[17] found that irradiation of an equimolar mixture of styrene and methyl methacrylate gave a copolymer containing 50.2% methyl methacrylate. If initiation had taken place primarily through the action of positive ions the product would be largely polystyrene, whereas if the initiator were a negative ion, the product would be largely poly (methyl methacrylate). The formation of a 50:50 copolymer is strong evidence of initiation by free radicals.

Free radicals may result from the decomposition of excited molecules produced either independent of ionization (2) or as a result of ionization (3 and 5). Reaction 8 depicts a free radical propagation step and reaction 9 depicts a free radical bi-molecular termination step. The nature of the free radical reactions is probably determined by the properties of the monomer units; since after the addition of several monomer units to the chain, the properties of the initiating free radical should be relatively unimportant. Accordingly, chain transfer, chain branching, and disproportionation reactions characteristic of the monomer system would be expected to occur.[13]

Charlesby[18] and Lawton et. al.,[19,20] found that polymers can be classified into two groups according to their behavior when exposed to pile radiation. They observed: (1) cross linking of the polymer chain leading first to an increase in molecular weight and, at high enough dose, to the formation of an insoluble network, or (2) scission of the molecular chains resulting in a decrease in average molecular weight. Both processes occur simultaneously in many polymers, i. e., polypropylene. Poly (methyl methacrylate) belongs to the second category.

The decrease in average molecular weight, namely, the viscosity decrease may be a general property of vinyl polymers with short side chains. If there are two side chains on alternate carbon atoms, as in poly-isobutylene or poly (methyl methacrylate), no minimum is observed, only a monotonic decrease in the intrinsic viscosity with dose.[21]

It has been pointed out[20] that all vinyl polymers have the structure:

$$\left[-CH_2 - \begin{matrix} R \\ | \\ C \\ | \\ R \end{matrix} - \right]_n$$

i. e., there is no hydrogen atom on the carbon bearing the side chain R but rather an α- substituent R', which may be CH_3, Cl, F,

etc. One obvious reason for this correlation is that the α-substituents, particularly if they are methyl groups, cause a steric strain which weakens the carbon-carbon bonds of the main chain. This is reflected in the heats of polymerization.

Bovey[8] has tabulated the heats of polymerization of several polymers, including methyl methacrylate. Table 3, taken from Wall's[22] paper includes data from several other sources.[23][24]

TABLE 3

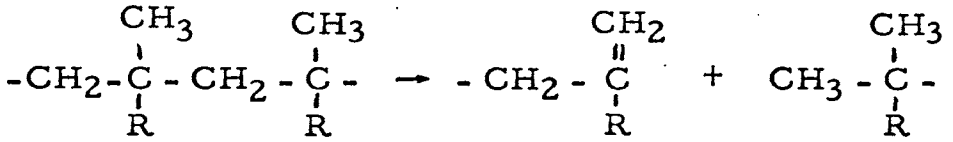
CORRELATION OF POLYMER PROPERTIES WITH EFFECT OF RADIATION

POLYMER	PREDOMINANT EFFECT OF RADIATION	HEAT OF POLYMERIZATION Kcal./mole monomer
Polyethylene	Crosslinking	22
Methyl acrylate	"	19
Acrylic acid	"	18.5
Styrene	"	17
Methacrylic acid	Scission	15.8
Isobutylene	"	10-13
Methyl Methacrylate	"	13
α-Methyl styrene	"	9

From the table it can be seen that the heat of polymerization of methyl methacrylate is 13 kcal per mole of monomer, which is comparatively low. When the heat of polymerization is low, the

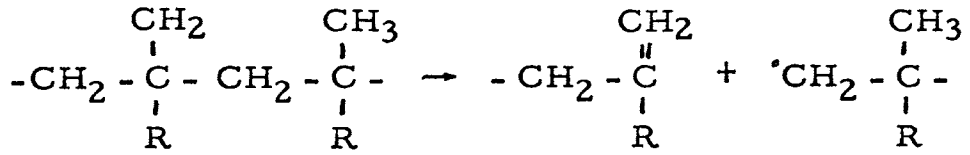
polymer tends to "unzip" readily to monomer during pyrolysis and to undergo scission as a result of irradiation.

It has been suggested[20] that the scission may occur by a rearrangement which will be easier when an α-methyl group is present



because of the proximity of the methyl and methylene groups.

Wall[22] has suggested that the initial step in the scission of alpha methyl substituted chains may be due to the abstraction of a hydrogen atom from the methyl group by a radical which is formed after ion pair formation. The resulting polymer radical then arranges:



This is not equivalent to the above formulation since a radical remains after each scission and can presumably initiate a further scission in the same manner which leads to the chain reaction.

All these suggested reactions are highly speculative and there is little or no direct evidence for any particular mechanism.

Indeed, it is unlikely that any general scheme can be drawn up and that instead each polymer must be studied as a separate case. Further theorizing will be reserved for the discussion of this study. Bovey[5] found that after certain periods of radiation time that samples of poly (methyl methacrylate) became yellow. This was not directly attributed to the scission reaction since those in the pile became much darker than those exposed to γ-radiation at equal extents of scission. The ultra-violet absorption showed a marked increase, with a peak at a wave length somewhere below 260 mμ. This indicated the formation of conjugated unsaturated structures. The presence of oxygen has been reported not to affect the rate of chain scission[25] and it is also believed that the presence of oxygen may even retard scission[26] in poly (methyl methacrylate) when exposed to ionizing radiation.

When poly(methyl methacrylate) rods were exposed to about 2 pile units of radiation at the pile temperature of 70 °C, bubbles were formed. This behavior is believed to be due to gases which are evolved by partial decomposition of the polymer during irradiation. If the specimen received subsequent heating, after being irradiated, above its softening point (100 °C - 125 °C) a foamed material was produced which would indicate that the gases are held in the polymer in a dissolved state under pressure. Higher doses both weakened the polymer and increased the quantity

of gas. It appears reasonable to assume that the gases were formed during the irradiation process rather than during the subsequent heating. This was shown by dissolving an irradiated but unfoamed specimen in chloroform where a considerable evolution of gas was observed.[6]

A mass spectrographic analysis of the gases gave (by volume):[6] H_2, 44.1%; CH_4, 6%; CO, 22.8%; CO_2, 18.8%; O_2, 0.3%; other hydrocarbons, 0.2%; miscellaneous peaks, probably corresponding to low alcohols and esters, 0.5%. Very similar results were obtained by Wall and Brown.[26] The formation of methane and of relatively large amounts of CO and CO_2 were assumed to be due to the fracture of the $-COOCH_3$ side chains, although the proportion of methane is less than one might expect on this basis. Since predominant decomposition of the main chain would give mostly hydrogen, plus some hydrocarbon higher than methane, it appears that most of the decomposition was suffered by the side chains.

It was assumed in the study by Alexander, Charlesby, and Ross[25] that poly(methyl methacrylate) undergoes only scission without any crosslinking. This assumption had been proven by Shultz, Roth, and Rathmann[27] to be the case. They found the weight average molecular weights, $\overline{Mw}$, determined by light

scattering, coincide with those determined by viscosity, $\overline{Mv}$. It might be concluded then that crosslinking with consequent formation of branched molecules in the irradiated polymer is negligible.

III. EXPERIMENTAL

The purpose of this investigation was to study the effect of gamma radiation on the rate of polymerization of methyl methacrylate monomer; and also to determine the effects of the presence of clay of known composition and of other solids on the rate of polymerization. Hereafter methyl methacrylate monomer will be referred to as MMA and poly(methyl methacrylate) will be referred to as PMMA.

A. Plan of Experimentation

A series of aluminum cells containing methyl methacrylate monomer was subjected to a controlled gamma flux for a predetermined period of time. Then the viscosity average molecular weight ($\overline{M}_V$) were determined by intrinsic viscosity measurements.

The preceding was repeated with the addition of varying amounts of clay of known chemical composition and other solids of varying particle sizes. In addition to determining the $\overline{M}_V$ of the polymer, x-ray diffraction patterns were made on the clay before and after irradiation.

B. Materials

The materials used in this investigation are tabulated in Appendix 1.

C. Apparatus

The apparatus used in this investigation is described in Appendix 2.

D. Irradiation Facilities

The nuclear training reactor (10 KW swimming pool, modified BSR-type), University of Missouri at Rolla, was utilized for the irradiation of the samples. The reactor core contains fuel elements, each of which contains ten fuel plates (MTR type). Each plate contains approximately 17 grams of 90% U-235 enriched uranium oxide. The moderator, reflector and coolant are light water. The biological shield is 21 feet of water and concrete. The samples were irradiated in grid positions D1 and E1 of the reactor with core loading 29 T. (see Figure 1, page 18). The dose rates (flux) received by the samples were measured with a Fricke (ferrous sulfate) dosimeter as D1: 4.22×10^5 rads/hr @ 10 kw.

E1: 5.56×10^5 rads/hr @ 10 kw.

E. Methods of Procedure

(1) Preparation of the samples

A burette was used to measure 32 ml. of methyl methacrylate monomer (32 ml. x 0.939 grams/ml. = 30 grams) into the aluminum cells. The caps were sealed in place by an amine cured epoxy resin. The samples were then placed in a

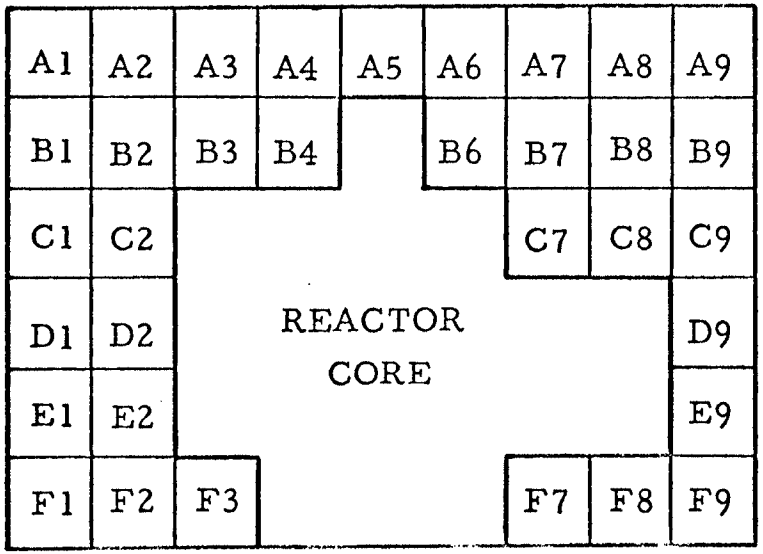


Figure 1. THE CORE CONFIGURATION

stand overnight to allow the curing of the epoxy resin at room temperature. Then an additional piece of pressure-sensitive tape was used to wrap around the cap to ensure that the container was water-proof. Figure 2, page 20 shows a completed sample cell. The samples containing Ajax P clay and other solids followed the same procedure except the amounts of clay and monomer were the same, 20 grams of each. The solids were incorporated into the monomer using a glass spatula and the mixture vibrated in order to remove air voids.

(2) Irradiation of the samples

The samples contained in the aluminum cells were held in position D1 and E1 by a cadmium lined plastic (Lucite) holder, shown in Figure 3, page 21. Their positions were centered vertically at a distance of 4.5 inches from the face of the core. The cadmium lining was used to shield against the thermal neutron activation. Fast neutrons were present but the dose rate from these should be much less than the dose from the gamma rays. The lower fast neutron flux was borne out by the low sample activation in the clay samples.

(3) The Fricke Dosimeter (28)

The most widely used chemical dosimeter for gamma radiation is the oxidation of ferrous ions to ferric in 0.8 normal

Figure 2. SAMPLE CONTAINER

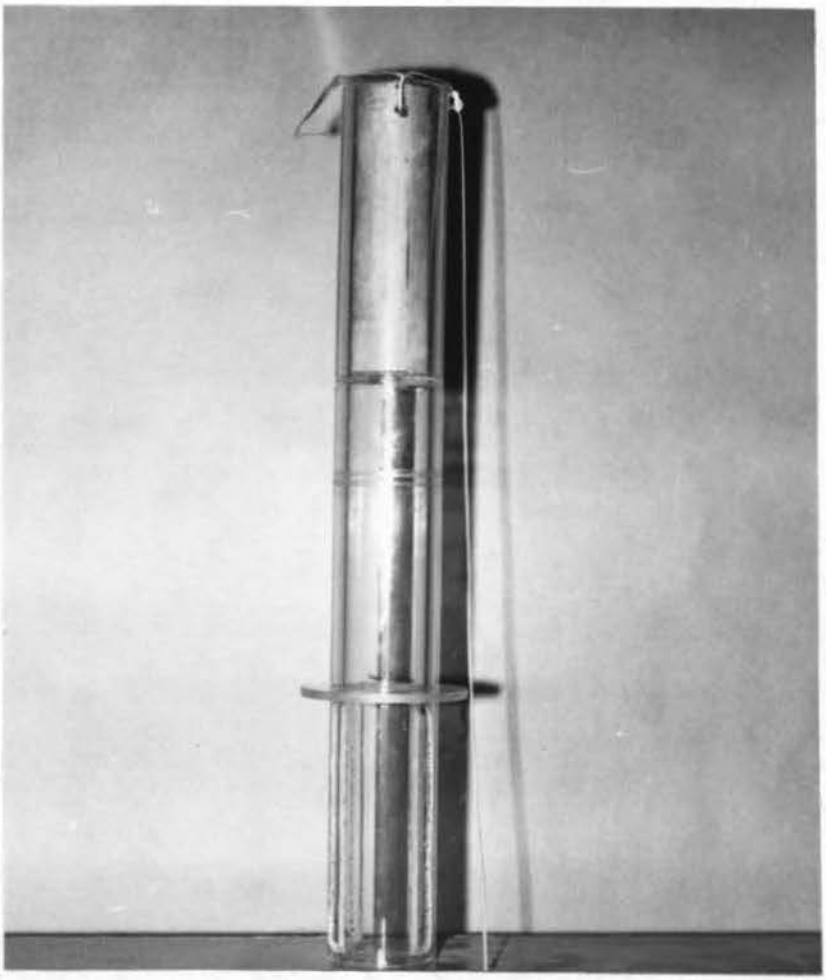


Figure 3. THE CELL ASSEMBLY

solution of sulfuric acid. The method is discussed in reference 28.

The dose rate is given by

$$R(\text{rads/hr}) = \frac{10^9}{\epsilon b Y t} (A_{\text{sample}} - A_{\text{blank}})$$

A = absorbancy of irradiated and unirradiated solution respectively.

ϵ = molar extinction coefficient.

Y = ferrous sulfate yield, micromolar of ferric ions per 1000 rads.

b = sample thickness.

t = irradiation time, hr.

The value of the constants used is ϵ = 2174 liter/(mole)(cm), Y = 15.5, b = 1 cm. and t = 20 minutes.

The ferrous sulfate solution was irradiated in the same positions as the samples but at lower power levels. The lower power used was due to the upper limit of the dosimeter. After irradiation the absorbancy was measured in a Beckman spectrophotometer and the above formula was used to determine the dose. The linearity of gamma dose with power was checked by irradiation at 267 and 2000 watts. The results were as follow:

D1: 4.22×10^5 rads/hr @ 10 kw.

E1: 5.56×10^5 rads/hr @ 10 kw.

(4) Testing of the Samples

After irradiation, the samples were removed from the aluminum cells and visually inspected for changes in color, viscosity as well as other changes. The samples were then photographed. The intrinsic viscosities of the polymerized samples were determined following the procedures outlined in Appendix 3 and the viscosity average molecular weight was determined on each sample. X-ray diffraction patterns were made on the clay before and after irradiation as outlined in Appendix 4.

IV. DATA AND RESULTS

The data and results obtained in this investigation are presented in the order of increasing radiation times. The results for the polymerized methyl methacrylate monomer alone are presented first followed by the results obtained for the mixtures of monomer and clay and other solids.

A. Irradiated MMA Monomer Samples

The viscosities of the samples irradiated for periods of time from 15 minutes up to 120 minutes remained as liquids and only the final viscosities were determined on the samples. The only observation made on these samples was that an increase in viscosity was noted with increasing irradiation time. Table 4, page 25 gives the results of the viscosity measurements and Figure 4, page 26, shows a plot of these data. Figures 5 and 6, page 27 show the appearance of samples after 15 minutes and 120 minutes of irradiation time. Both of the samples were shaken thoroughly prior to taking the photographs. Entrapped air bubbles which are indicative of the viscosity increase can be seen in Figure 6.

Samples which had been irradiated for 180 minutes were characterized by a sticky gel at the bottom of the aluminum cells and a very viscous liquid in the upper portion of the cell. Figure 7,

TABLE 4. VISCOSITY DATA FOR LIQUID SAMPLES

Sample No.	Irradiation Time (minutes)	Irradiation Flux (rads/hr)	Average Efflux Time (seconds) @ 30 °C	Viscosity in Centistoke @ 30 °C
Monomer	0	0	69.2	$\nu = \frac{\eta}{\rho} = At - B/t = 0.5230$*
1	15	4.22×10^5	69.3	0.5238
2	15	"	69.3	
3	30	"	69.5	0.5256
4	30	"	69.5	
5	45	"	108.4	0.8502
6	45	"	86.2	
7	60	"	173.3	1.3719
8	60	"	171.3	
9	120	"	2504	A't = 259.4

* A = 0.00806, B = 2.30981, t = Efflux Time, A' = 0.1036

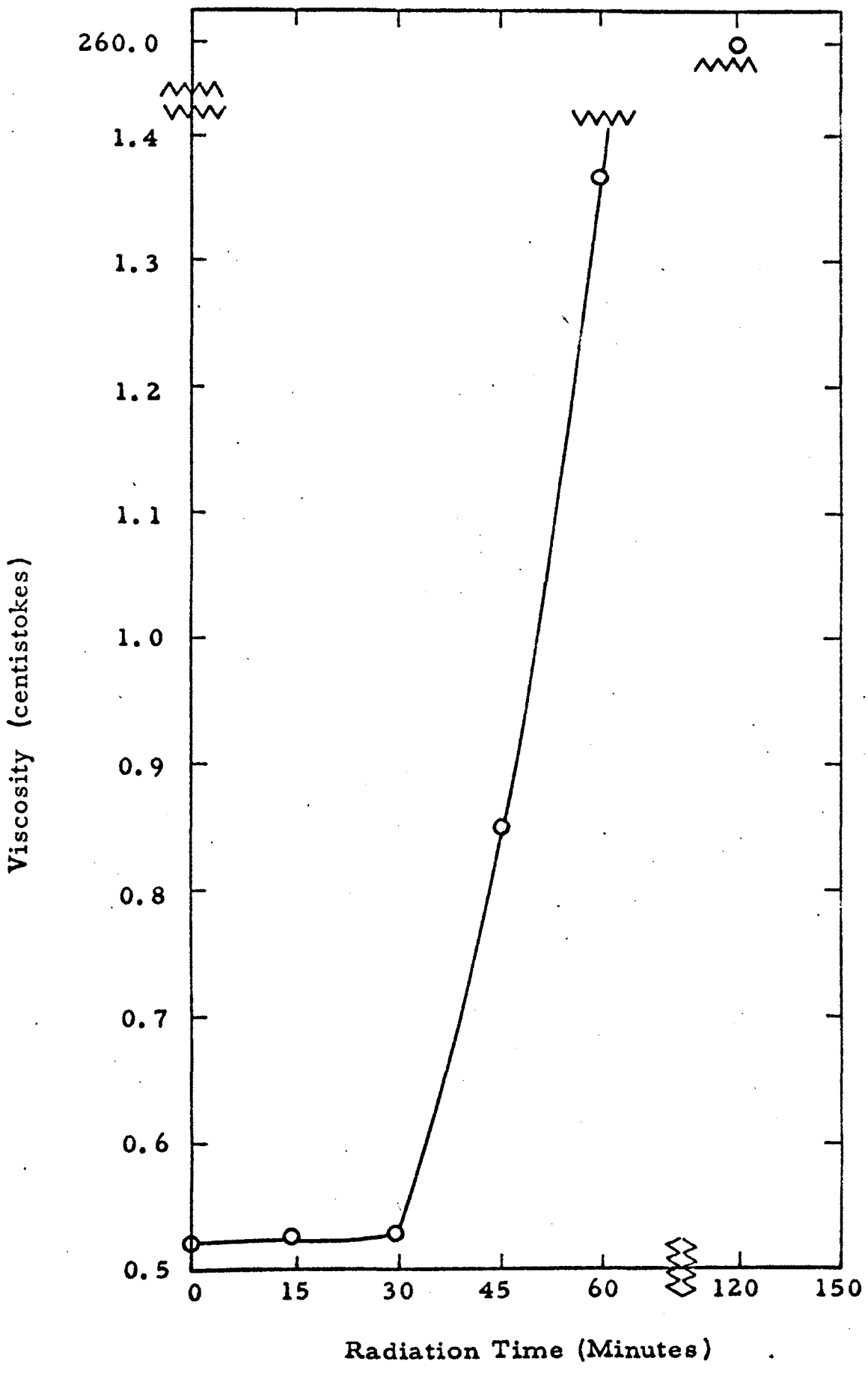


Figure 4. RADIATION TIME vs. VISCOSITY OF LIQUID

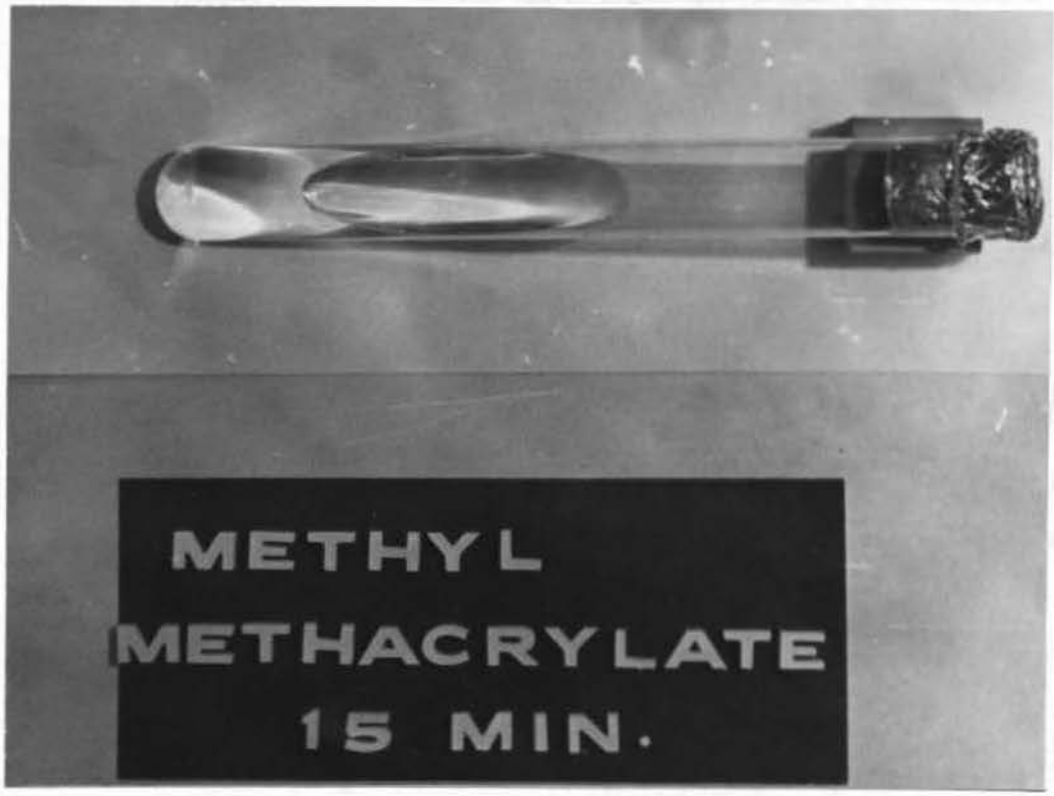


Figure 5. SAMPLE No. 1 AFTER 15 MINUTES OF GAMMA RADIATION

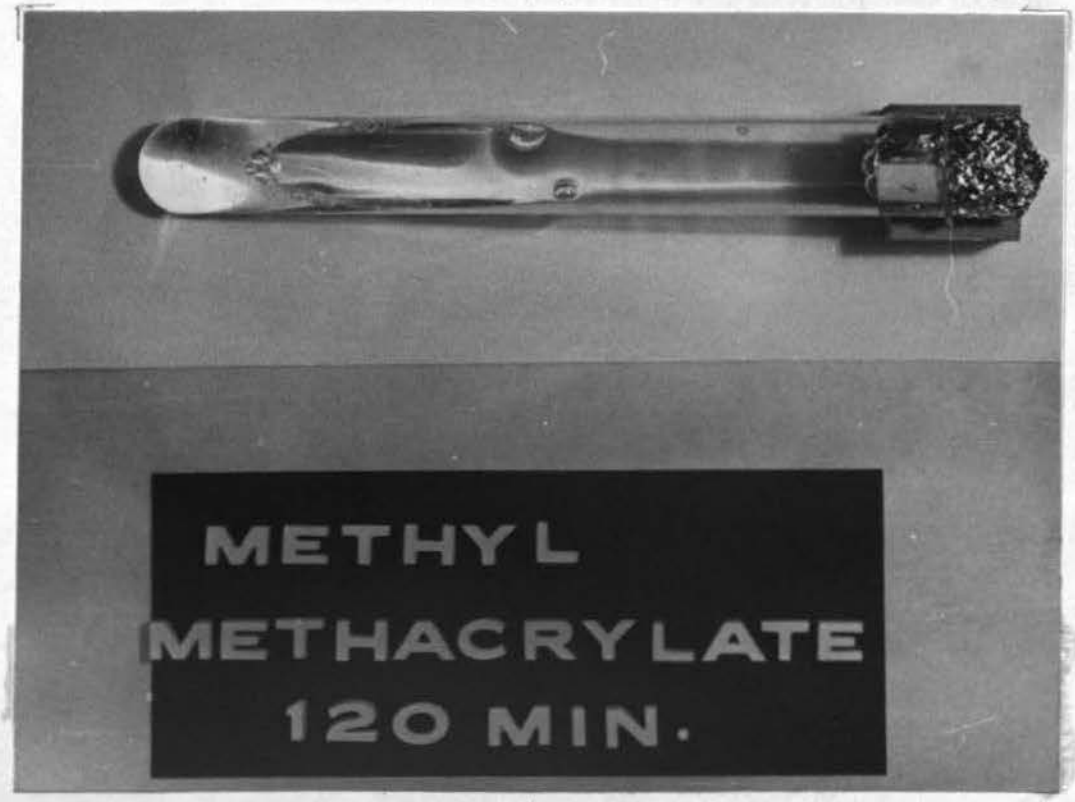


FIGURE 6. SAMPLE No. 9 AFTER 120 MINUTES OF GAMMA RADIATION

Figure 7. SAMPLE No. 10 AFTER 180 MINUTES OF GAMMA RADIATION

page 28 shows this phenomenon. Reduced viscosities were determined for the polymer in both the upper and lower portions of the cell. These data are plotted in Table 5, page 30, and are plotted in Figures 8 and 9, pages 31 and 32.

Samples irradiated for 240 minutes were completely gelled and contained a hard colorless transparent solid at the bottom and a rubbery gel at the top. This is shown in Figure 10, page 33. Reduced viscosities were determined for the polymer in both the upper and lower portion of the cell. These data are presented in Table 6, page 34, and are plotted in Figures 11 and 12, pages 35 and 36.

Samples irradiated for 480, 720, 1440 and 2880 minutes were all solids but were progressively discolored from a light yellow after 480 minutes to a brownish yellow after 2880 minutes. These samples were then tested at both ends as previously described. Photographs of the samples after 480, 720, and 2880 minutes are shown in Figures 13, 14 and 15, pages 37 and 38. The results of reduced viscosity measurements are given in Tables 7, 8, 9 and 10, page 39, 42, 45, and 48, and are plotted in Figures 16, 17, 18, 19, 20, 21, 22, and 23, pages 40, 41, 43, 44, 46, 47, 49, and 50. As would be expected, the $\overline{M}_v$ increases to a maximum and then begins to decrease due to polymer degradation. The $\overline{M}_v$ of the

TABLE 5. REDUCED VISCOSITY AS A FUNCTION OF CONCENTRATION FOR SAMPLE No. 10

Top of Sample

Concentration (grams/100 ml)	Density (grams/ml^3) @ 30°C	Average Efflux Time (seconds)	Viscosity Centipoise) @ 30°C	Reduced Viscosity
0.6828	1.2416	89.7	0.8657	0.3710
0.3414	1.2245	81.7	0.7717	0.3544
0.2276	1.2189	79.3	0.7435	0.3310
0.1707	1.2160	78.0	0.7285	0.3204
0.1366	1.2143	77.3	0.7203	0.3136
Bottom of Sample				
0.5802	1.2442	205.5	2.0468	3.3840
0.2901	1.2259	129.3	1.2556	2.8194
0.1934	1.2197	108.2	1.0377	2.5975
0.1451	1.2166	99.5	0.9475	2.4855
0.1160	1.2148	94.5	0.8956	2.4150

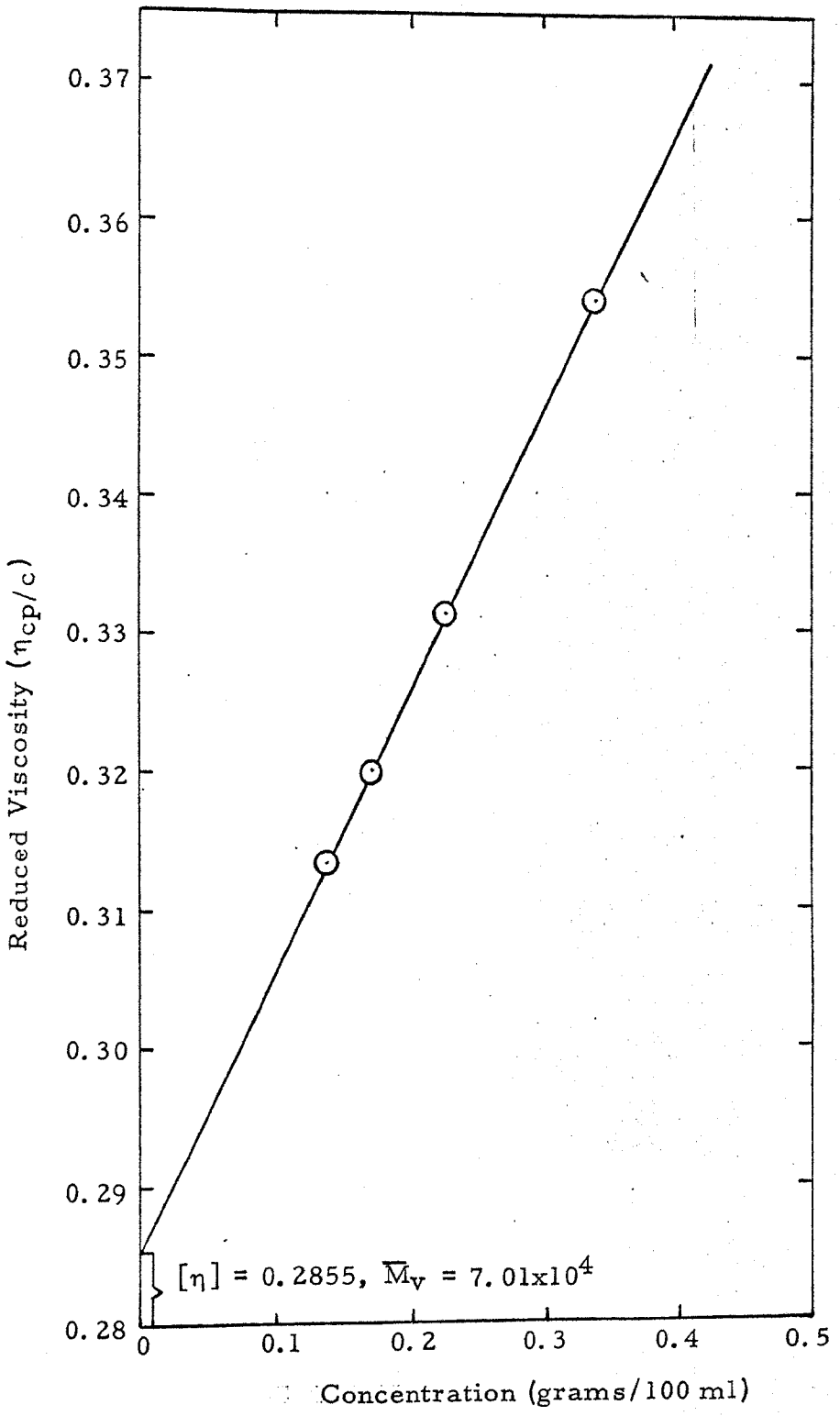


Figure 8. INTRINSIC VISCOSITY DETERMINATION FOR THE TOP PART OF SAMPLE NO. 10

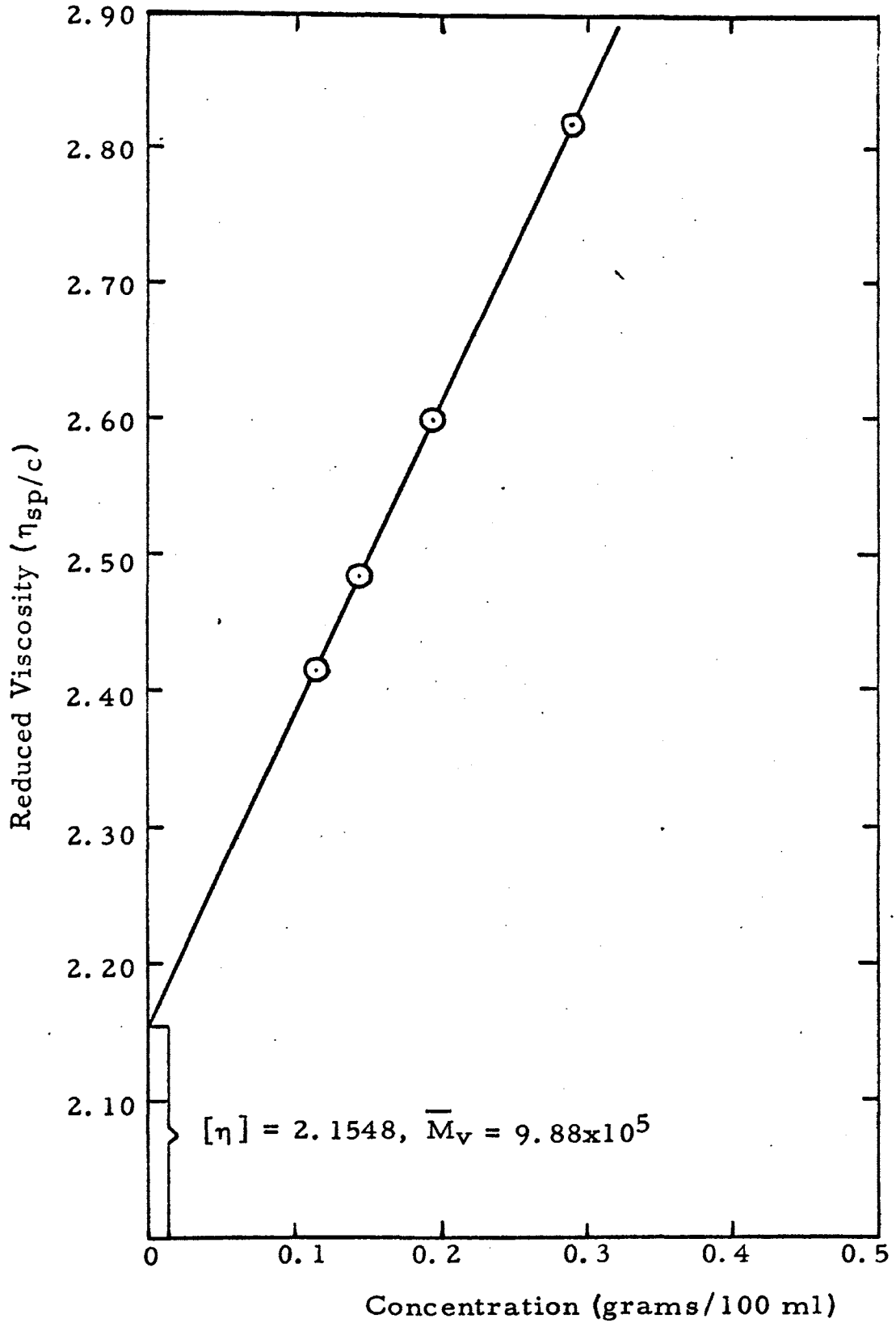


Figure 9. INTRINSIC VISCOSITY DETERMINATION FOR THE BOTTOM PART OF SAMPLE No. 10

Figure 10. SAMPLE No. 11 AFTER 240 MINUTES OF GAMMA RADIATION

TABLE 6. REDUCED VISCOSITY AS A FUNCTION OF CONCENTRATION FOR No. 11

Concentration (grams/100 ml)	Density (grams/ml^3) @ 30°C	Average Efflux Time (seconds)	Viscosity Centipoise) @ 30°C	Reduced Viscosity
Top of Sample				
0.4970	1.2417	114.6	1.1219	1.2561
0.2485	1.2246	93.0	0.8875	1.1462
0.1657	1.2189	86.5	0.8173	1.1060
0.1243	1.2161	83.4	0.7838	1.0840
0.0994	1.2143	82.0	0.7684	1.1314
Bottom of Sample				
0.7293	1.2429	290.4	7.8993	4.3845
0.3647	1.2252	159.2	1.5543	3.4290
0.2431	1.2193	126.0	1.2159	3.1350
0.1823	1.2164	111.4	1.0669	2.9875
0.1459	1.2146	103.0	0.9811	2.8823

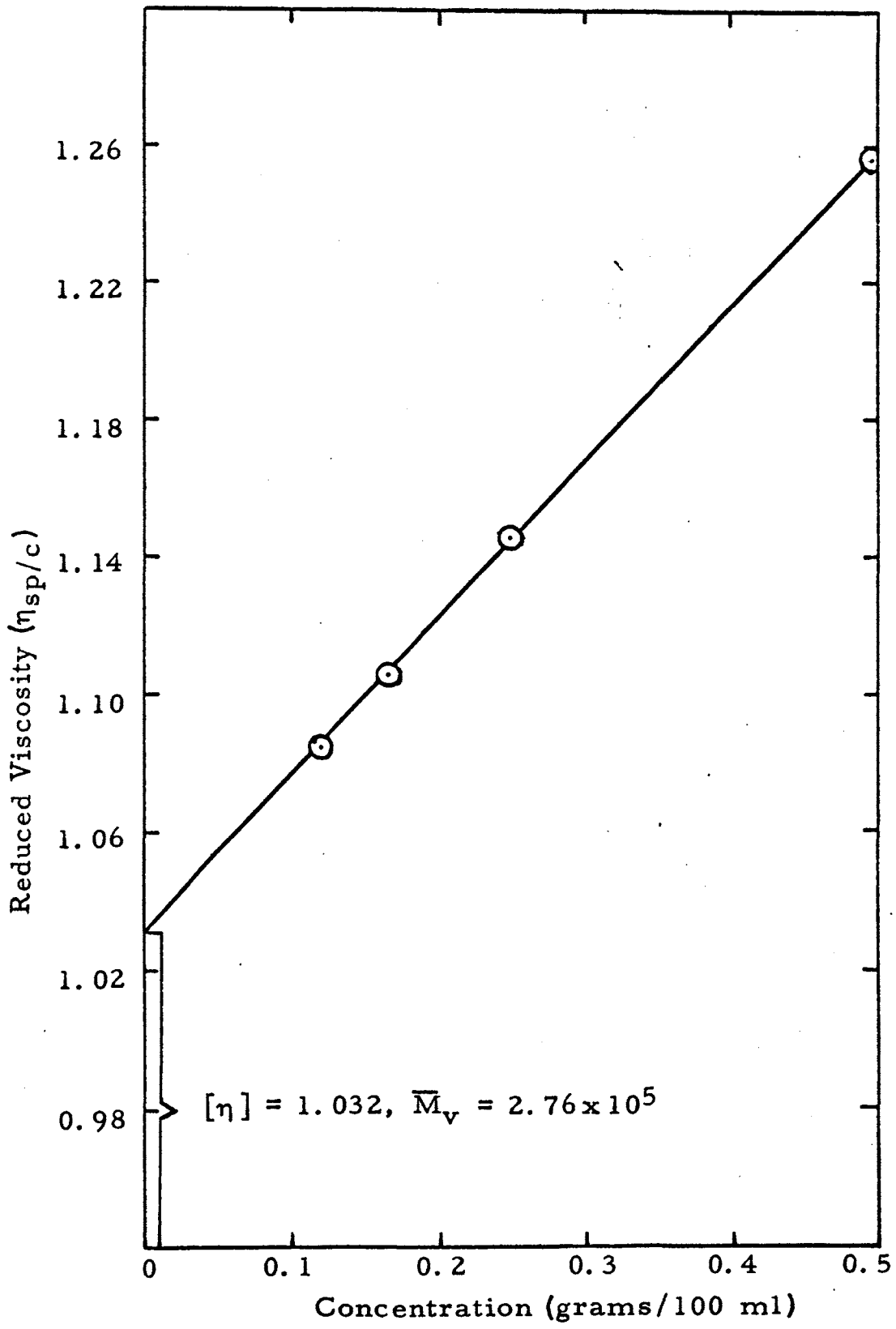


Figure 11. INTRINSIC VISCOSITY DETERMINATION FOR THE TOP PART OF SAMPLE No. 11

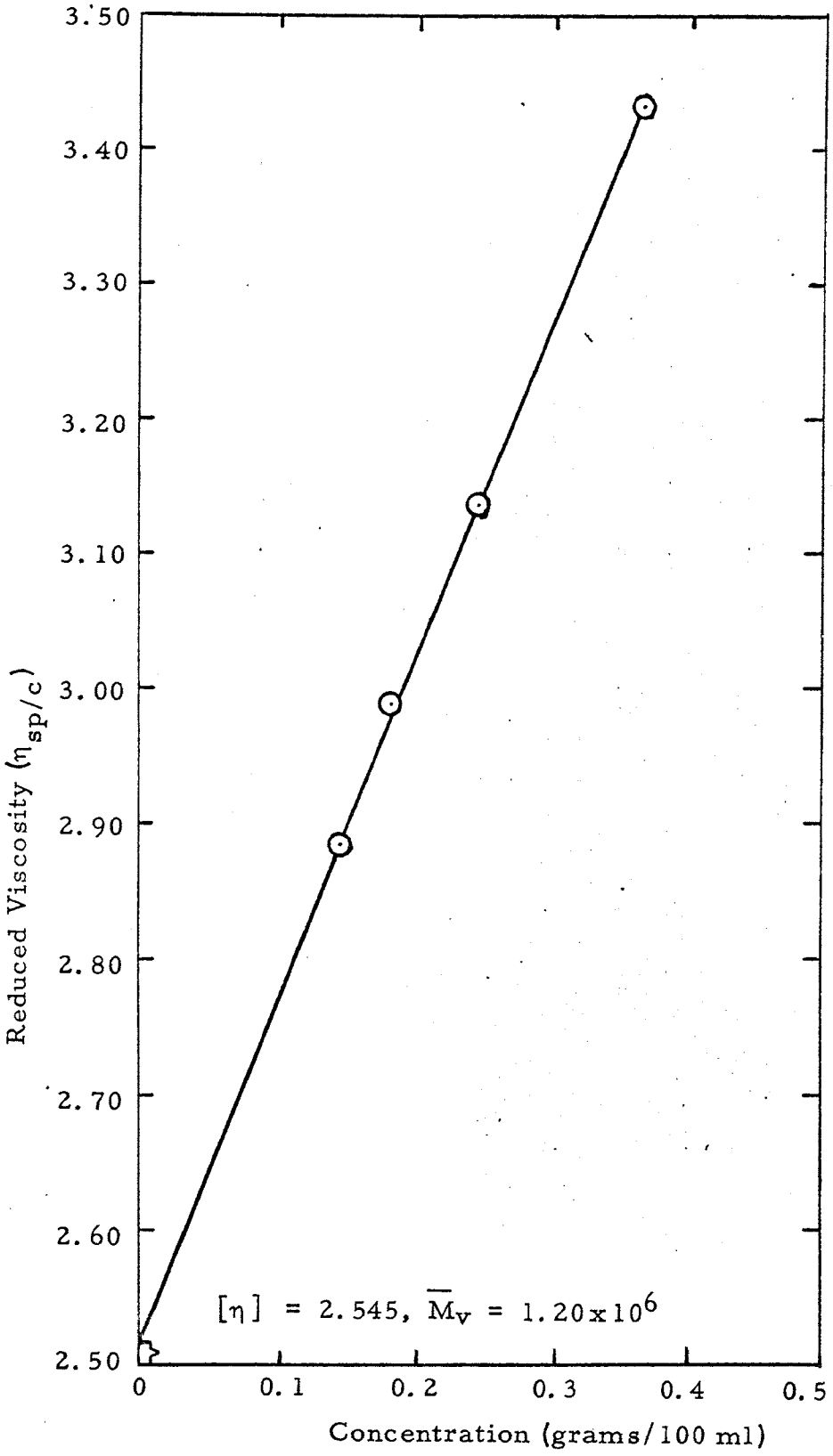


Figure 12. INTRINSIC VISCOSITY DETERMINATION FOR THE BOTTOM PART OF SAMPLE No. 11

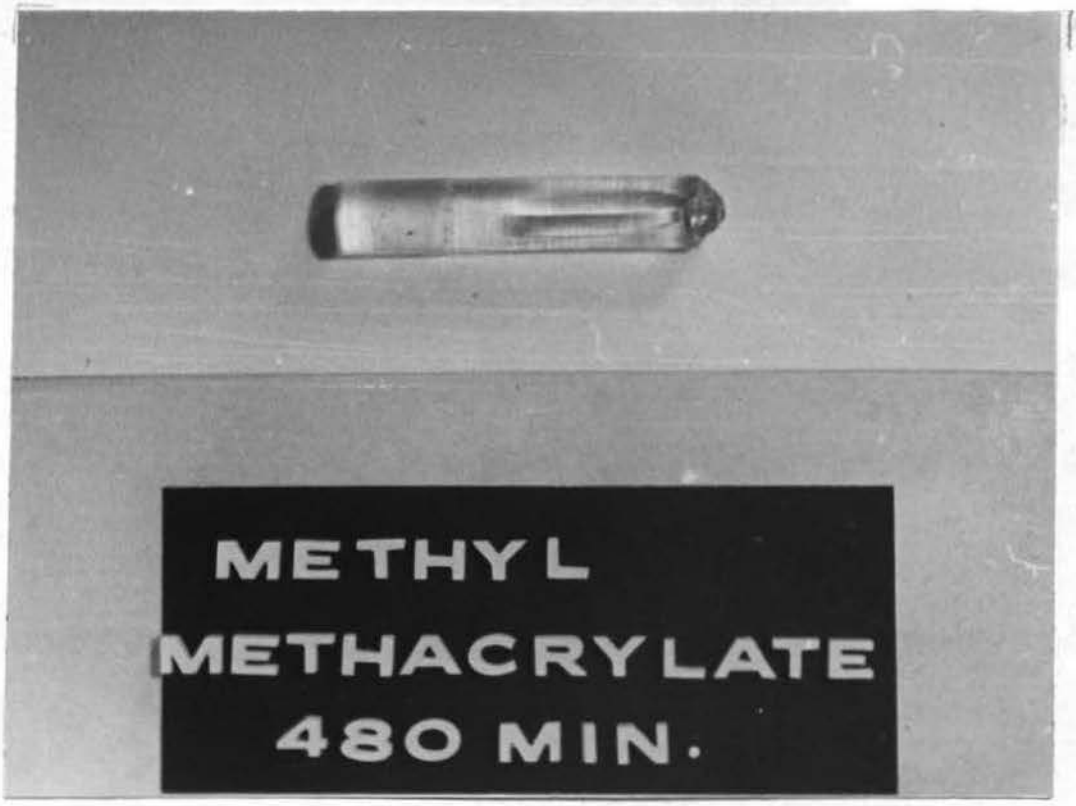


Figure 13. SAMPLE No. 12 AFTER 480 MINUTES OF GAMMA RADIATION

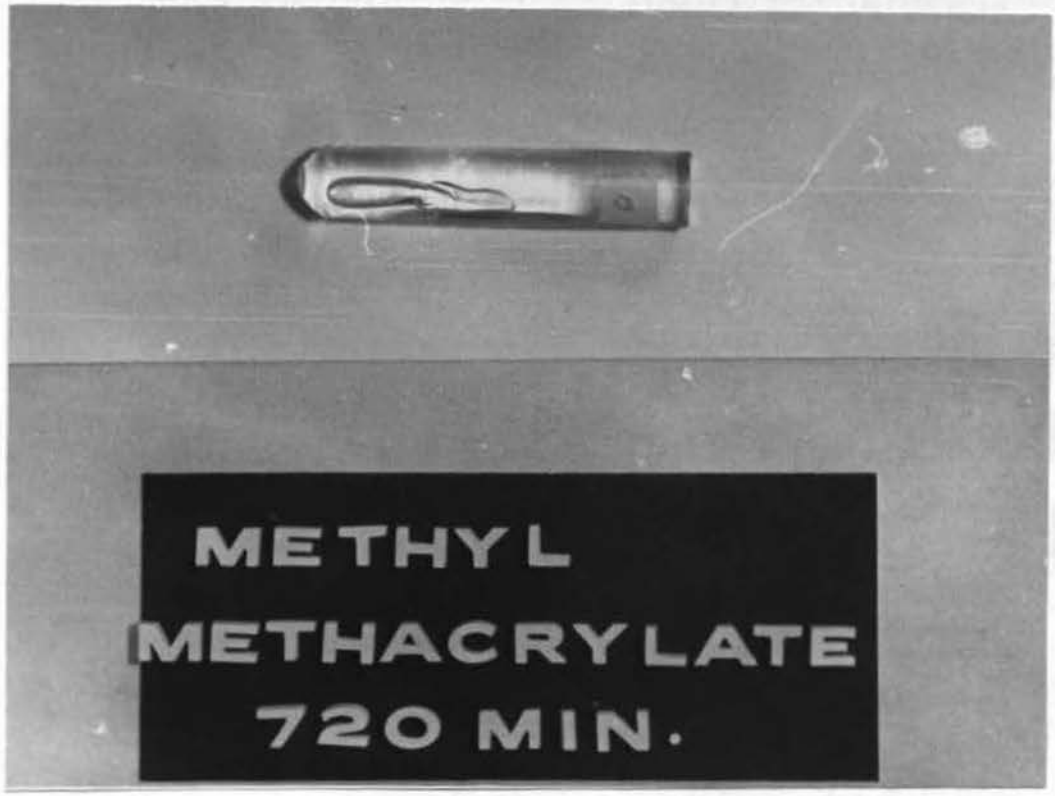


Figure 14. SAMPLE No. 13 AFTER 720 MINUTES OF GAMMA RADIATION

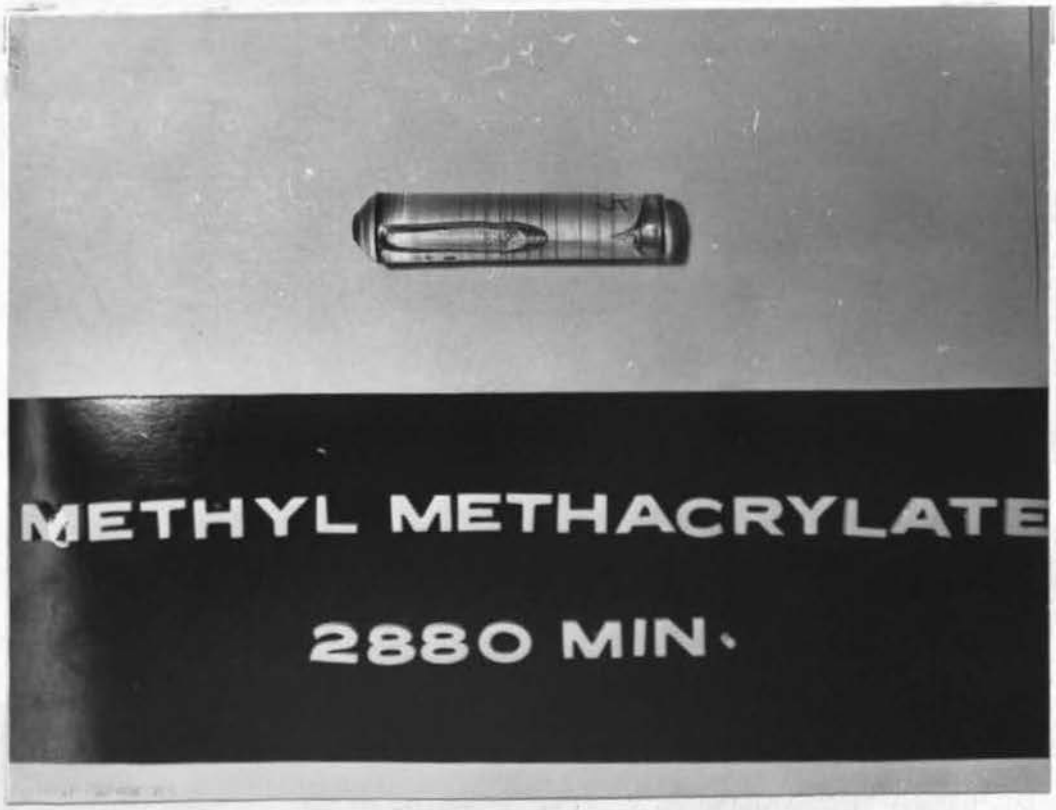


Figure15. SAMPLE No. 15 AFTER 2880 MINUTES OF GAMMA RADIATION

TABLE 7. REDUCED VISCOSITY AS A FUNCTION OF CONCENTRATION FOR No. 12

Top of Sample

Concentration (grams/100 ml)	Density (grams/ml^3) @ 30°C	Average Efflux Time (seconds)	Viscosity (Centipoise) @ 30°C	Reduced Viscosity
0.4967	1.2436	143.2	1.4153	2.1121
0.2484	1.2256	109.2	1.0527	1.9680
0.1656	1.2195	97.3	0.9275	1.9175
0.1242	1.2165	90.2	0.8533	1.8955
0.0993	1.2147	86.9	0.8185	1.8683
Bottom of Sample				
0.2857	1.2427	105.4	1.0285	1.7117
0.1429	1.2251	89.2	0.8491	1.6050
0.0952	1.2192	84.6	0.7981	1.5703
0.0714	1.2163	82.5	0.7747	1.5520
0.0571	1.2145	81.8	0.7665	1.5442

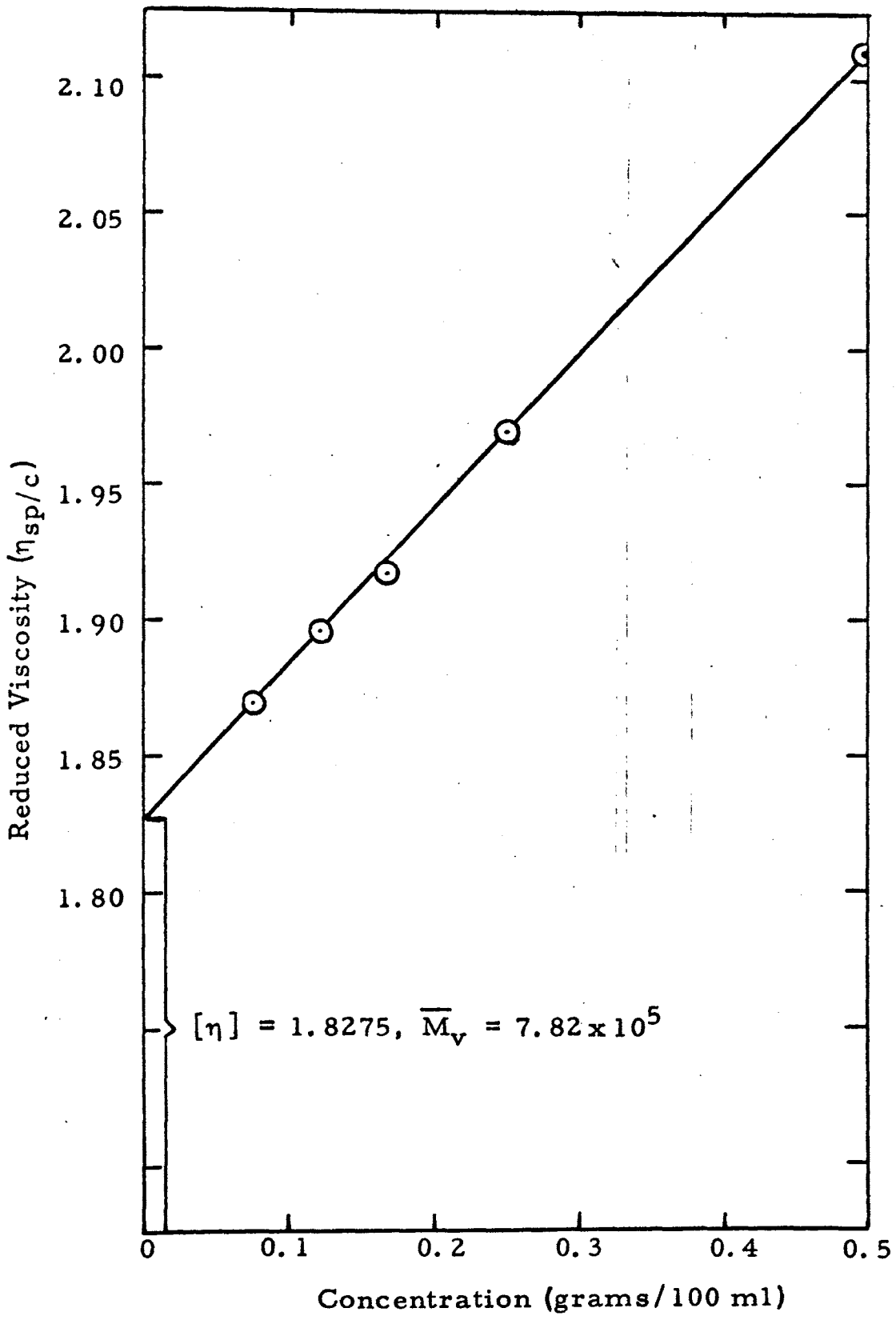


Figure 16. INTRINSIC VISCOSITY DETERMINATION FOR THE TOP PART OF SAMPLE No. 12

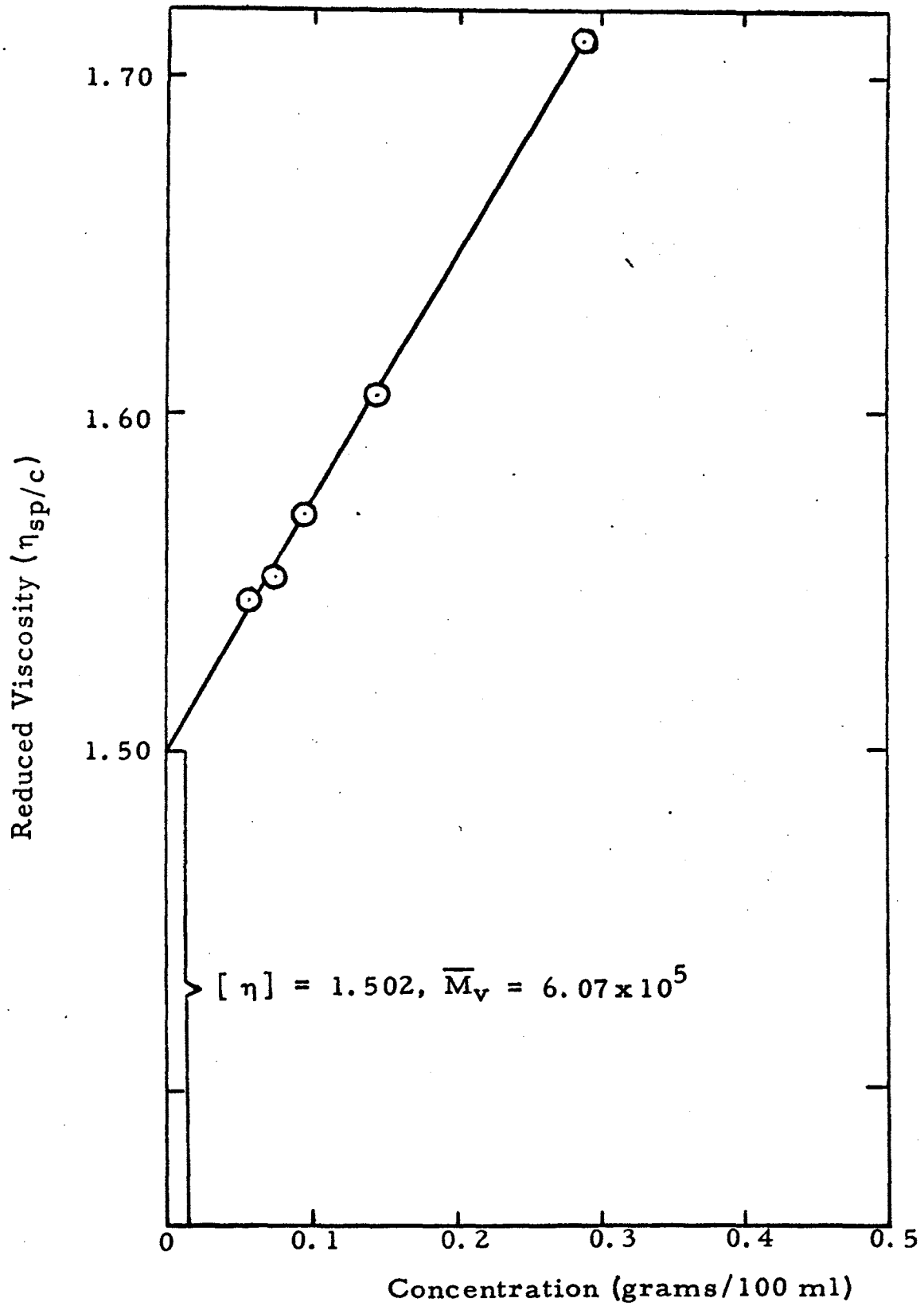


Figure 17. INTRINSIC VISCOSITY DETERMINATION FOR THE BOTTOM PART OF SAMPLE No. 12

TABLE 8. REDUCED VISCOSITY AS A FUNCTION OF CONCENTRATION FOR No. 13

Top of Sample

Concentration (grams/100 ml)	Density (grams/ml^3) @ 30°C	Average Efflux Time (seconds)	Viscosity (Centipoise) @ 30°C	Reduced Viscosity
0.4014	1.2439	105.1	1.0264	1.2108
0.2007	1.2257	92.4	0.8822	1.3814
0.1338	1.2196	84.5	0.7973	1.1537
0.1004	1.2166	82.0	0.7698	1.1455
0.0803	1.2148	80.3	0.7513	1.0926
Bottom of Sample				
0.9732	1.2435	158.7	1.5725	1.3118
0.4866	1.2255	113.2	1.0931	1.1974
0.3244	1.2195	98.1	0.9355	1.0927
0.2433	1.2165	92.0	0.8715	1.0421
0.1946	1.2147	88.6	0.8358	1.0091

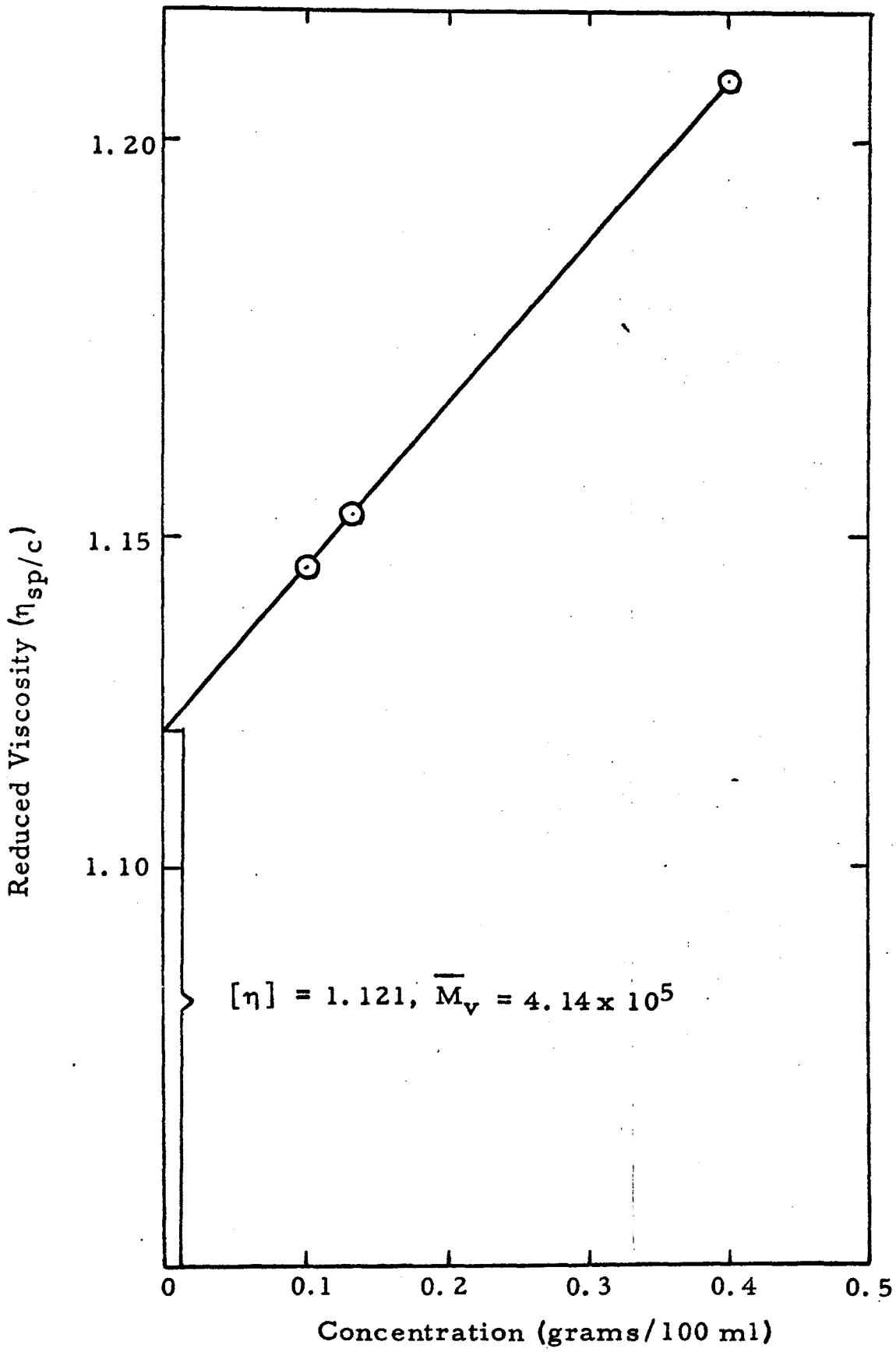


Figure 18. INTRINSIC VISCOSITY DETERMINATION FOR THE TOP PART OF SAMPLE No. 13

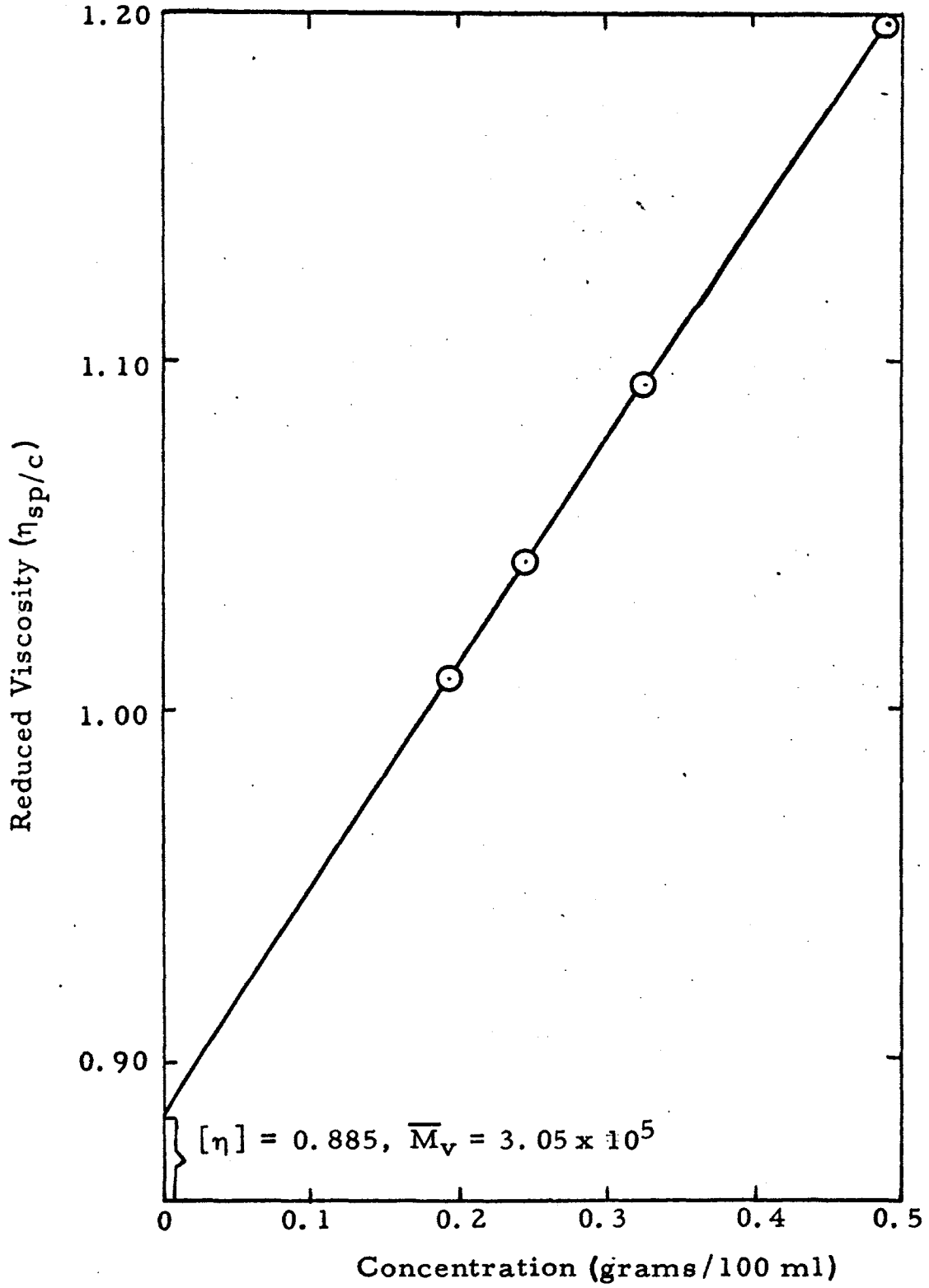


Figure 19. INTRINSIC VISCOSITY DETERMINATION FOR THE BOTTOM PART OF SAMPLE No. 13

TABLE 9. REDUCED VISCOSITY AS A FUNCTION OF CONCENTRATION FOR No. 14

Top of Sample

Concentration (grams/100 ml)	Density (grams/ml^3) @ 30°C	Average Efflux Time (seconds)	Viscosity (Centipoise) @ 30°C	Reduced Viscosity
0.8052	1.2445	109.2	1.0690	0.6803
0.4026	1.2260	90.4	0.8620	0.6159
0.2684	1.2198	84.9	0.8015	0.5949
0.2013	1.2168	82.6	0.7760	0.6137
0.1610	1.2149	80.8	0.7565	0.5913
Bottom of Sample				
1.1404	1.2455	139.4	1.3788	0.8735
0.5702	1.2265	103.6	0.9968	0.7772
0.3801	1.2202	94.8	0.9026	0.8070
0.2851	1.2170	89.6	0.8475	0.7963
0.2281	1.2151	86.5	0.8147	0.7895

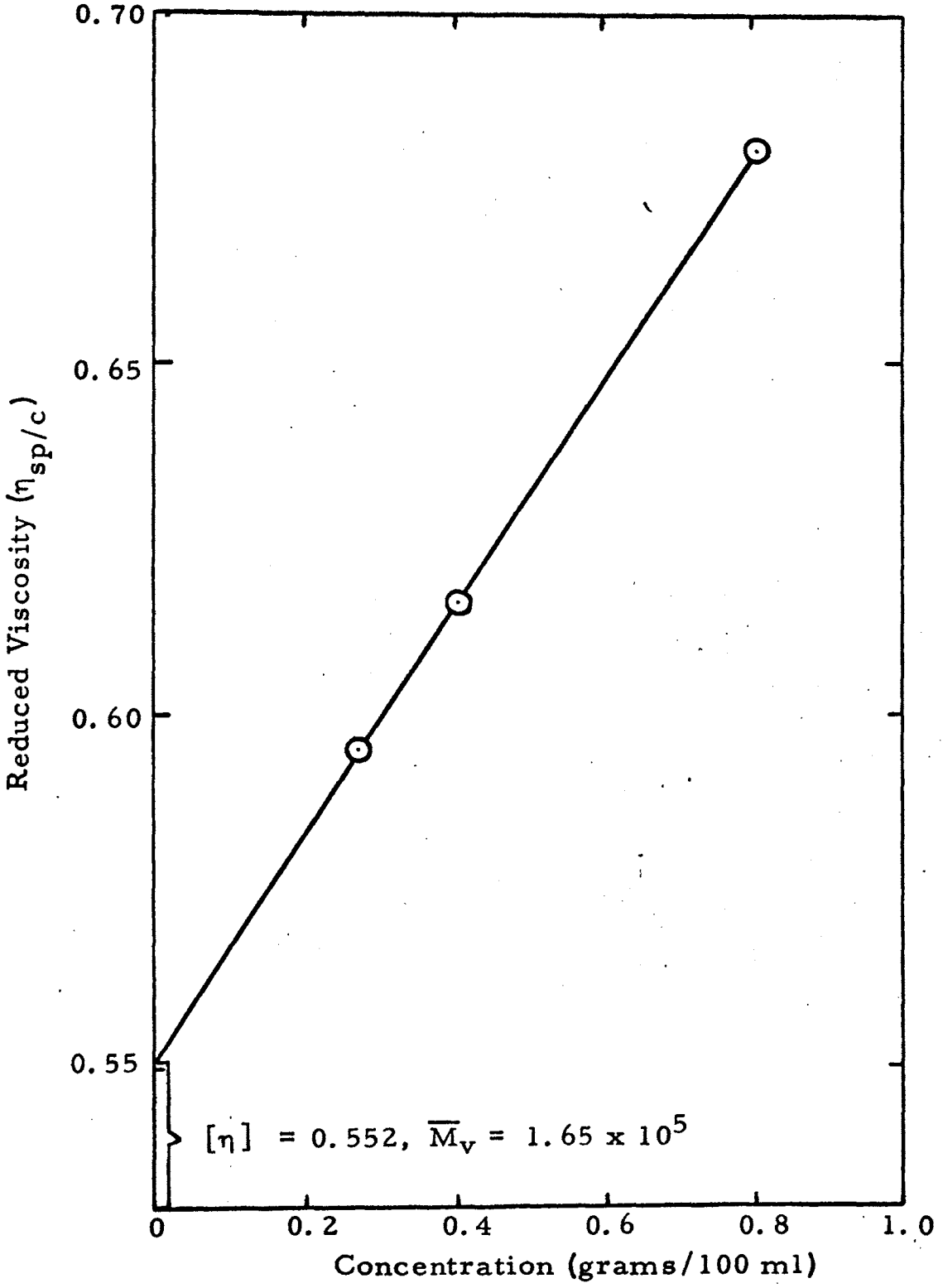


Figure 20. INTRINSIC VISCOSITY DETERMINATION FOR THE TOP PART OF SAMPLE No. 14

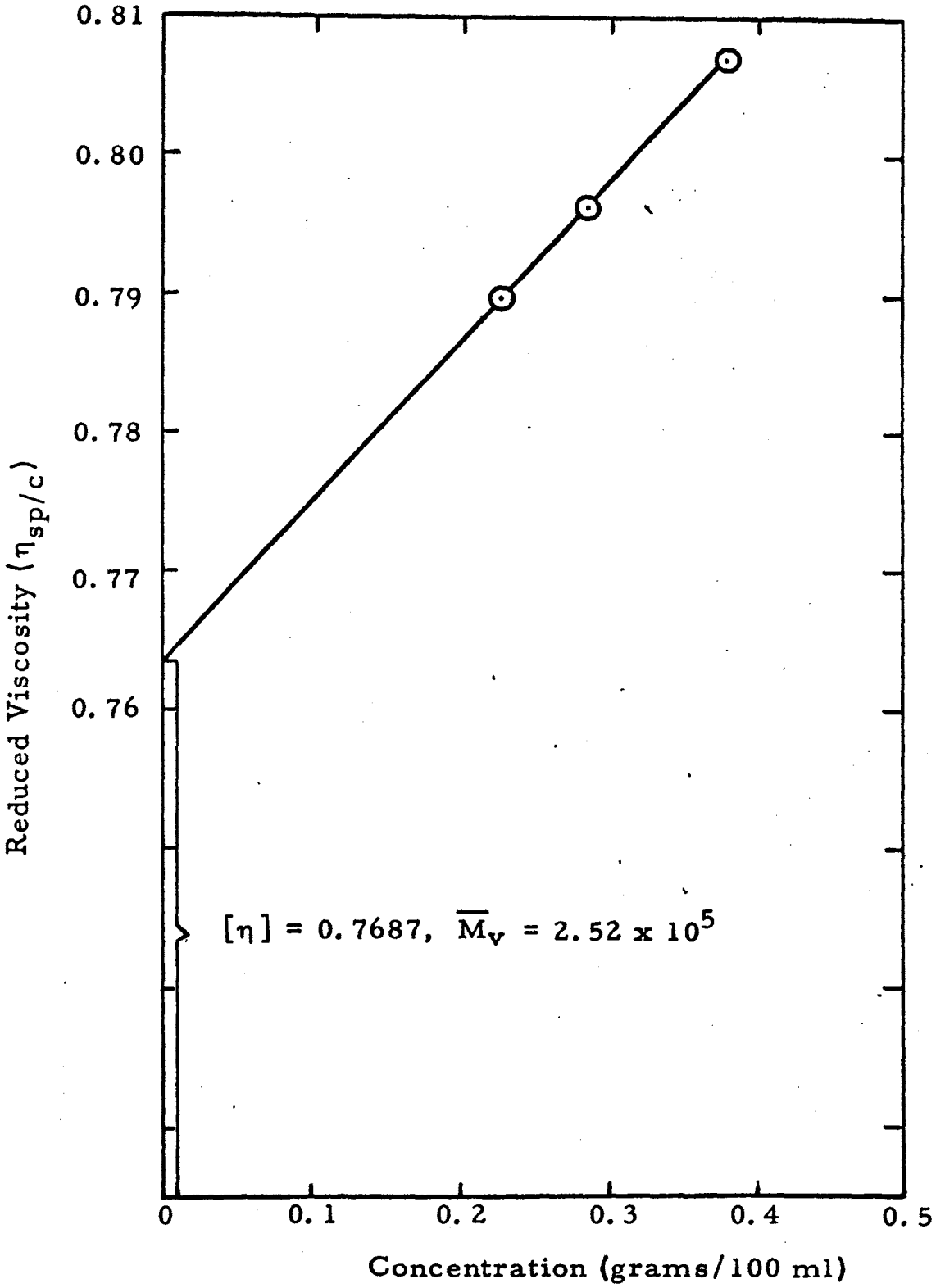


Figure 21. INTRINSIC VISCOSITY DETERMINATION FOR THE BOTTOM PART OF SAMPLE No. 14

TABLE 10. REDUCED VISCOSITY AS A FUNCTION OF CONCENTRATION FOR No. 15

Top of Sample

Concentration (grams/100 ml)	Density (grams/ml^3) @ 30°C	Average Efflux Time (seconds)	Viscosity (Centipoise) @ 30°C	Reduced Viscosity
1.2204	1.2447	107.5	1.0517	0.4283
0.6102	1.2261	92.3	0.8815	0.4526
0.4068	1.2199	85.1	0.8036	0.4019
0.3051	1.2168	81.6	0.7658	0.3566
0.2441	1.2149	80.3	0.7514	0.3371
Bottom of Sample				
0.8708	1.2450	99.2	0.9665	0.4585
0.4354	1.2263	86.5	0.8222	0.4372
0.2903	1.2200	82.3	0.7750	0.4206
0.2177	1.2169	80.2	0.7516	0.4119
0.1742	1.2150	79.3	0.7412	0.4019

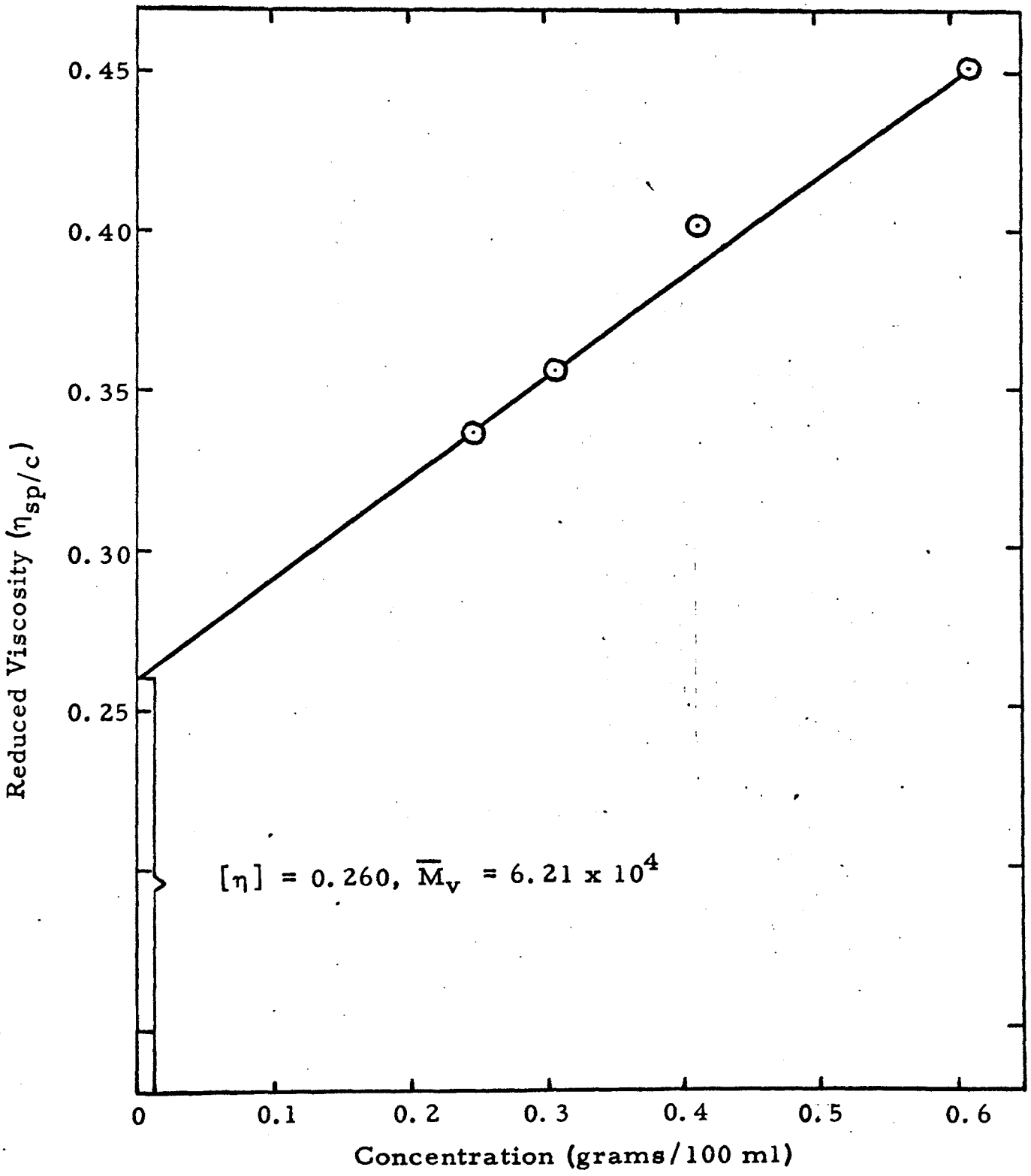


Figure 22. INTRINSIC VISCOSITY DETERMINATION FOR THE TOP PART OF SAMPLE No. 15

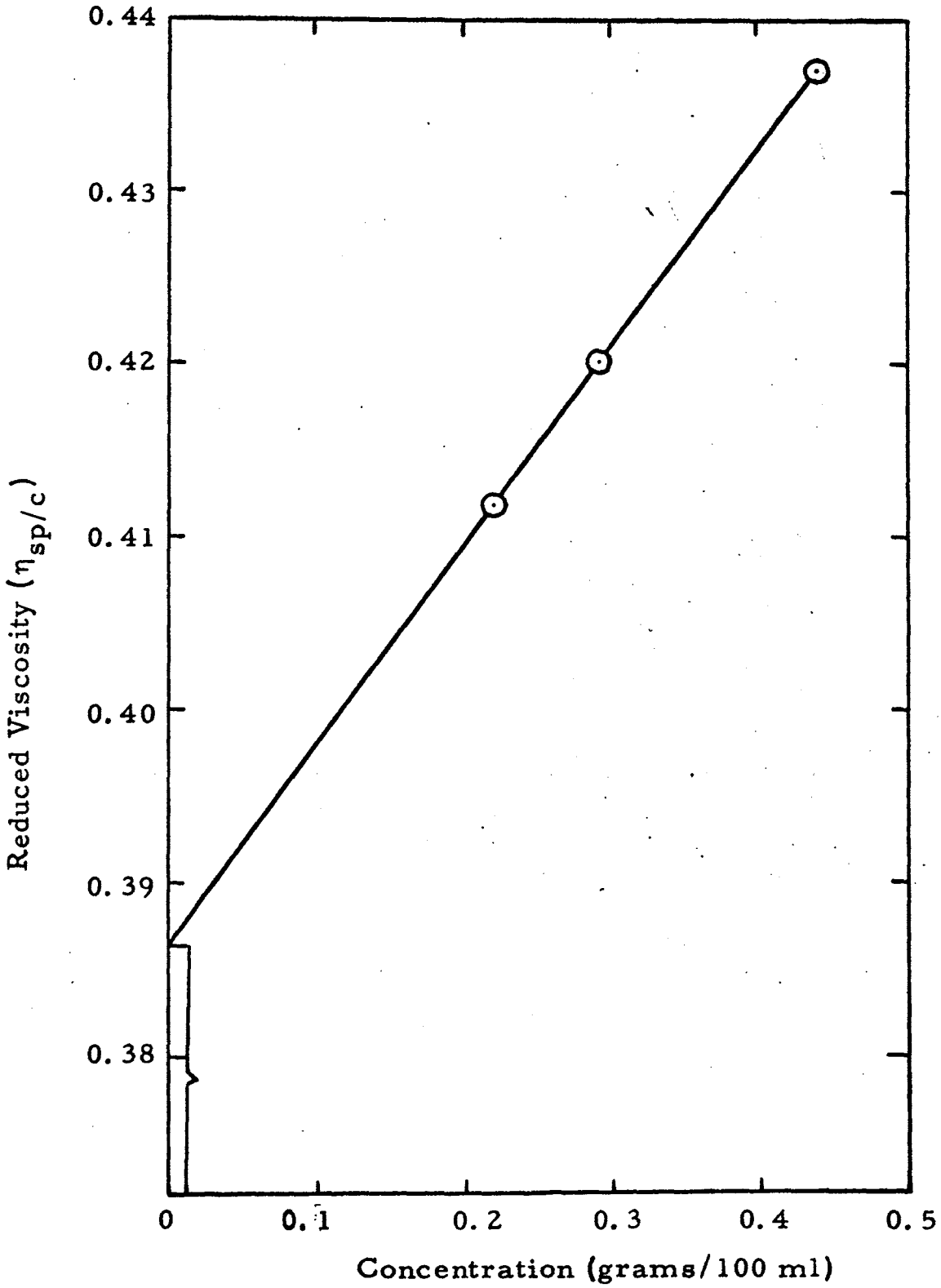


Figure 23. INTRINSIC VISCOSITY DETERMINATION FOR THE BOTTOM PART OF SAMPLE No. 15

bottom portions of the samples increase at a faster rate than the top portions but they also begin to decompose sooner. This behavior will be explained in the discussion section. $\overline{M}_v$ is plotted vs radiation time in Figure 24, page 52. The dotted lines are the extension of the curve to zero radiation time.

It was noted that the aluminum cells which were used for all of the above samples were slightly distorted. When they were removed from the reactor pool and after the cells had been cut away from the samples the solid samples showed identical distortions. This indicates that the cells were distorted while in the reactor pool. Qualitative calculations indicate that there is sufficient pressure in the pool at a depth of 22 feet to cause the cells to distort slightly. It was also noted that several cavities appeared on the side surfaces of these samples. Possible causes of the formation of these cavities will be taken up in the discussion section of the thesis.

B. Irradiated MMA Monomer-Clay Samples

With a 1:1 weight ratio of monomer to clay (particle size 2 microns) a stable paste is formed. Irradiated samples of this monomer-clay mixture were converted from the monomer to the polymer in a very short time compared to results obtained for the monomer alone.

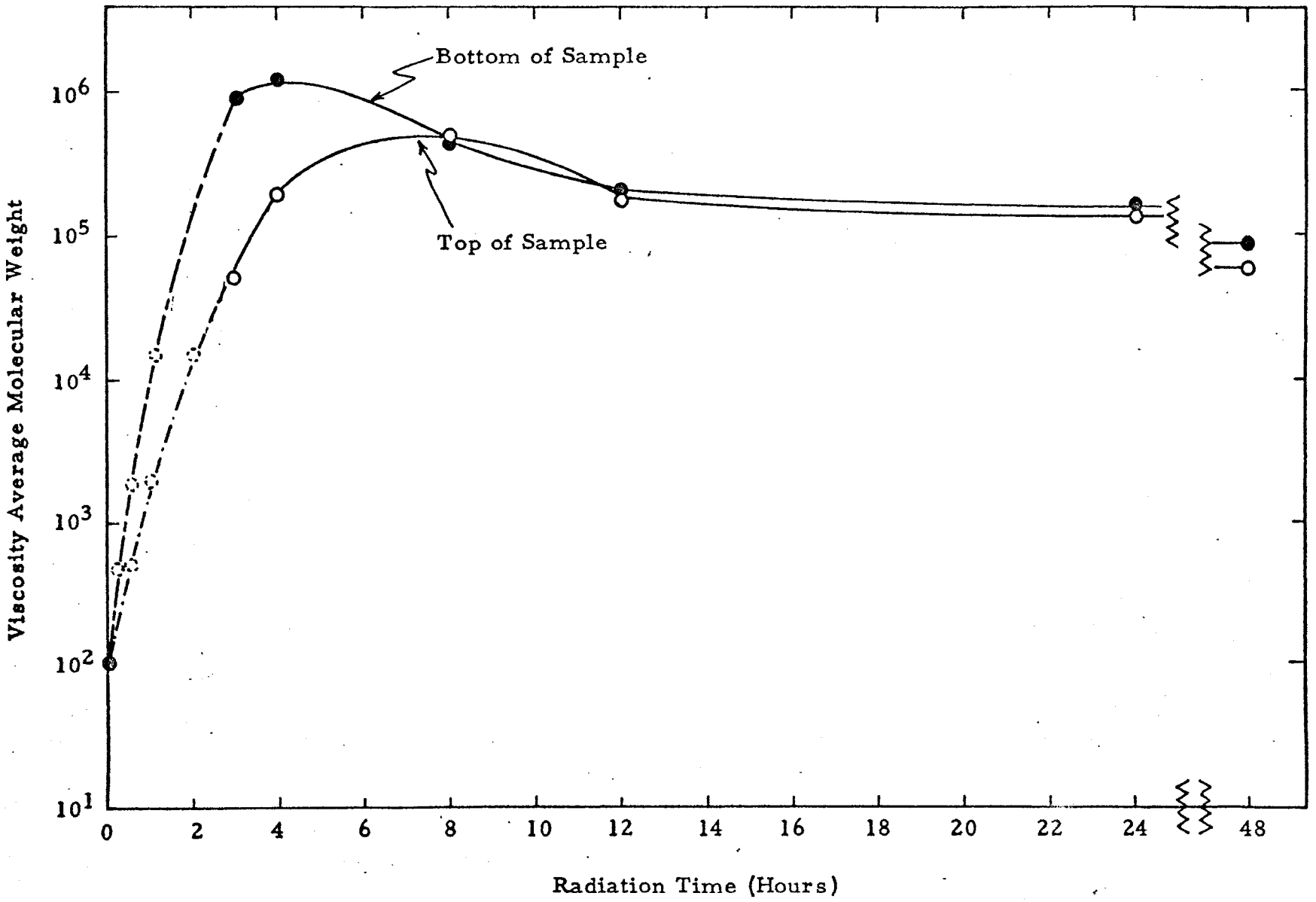


Figure 24. RADIATION TIME vs $\overline{M}_v$

A solid product is formed after 15 minutes of irradiation time. Figures 25, 26, 27, and 28, pages 54 and 55, show the appearance of samples after 15, 30, 720, and 1440 minutes of irradiation time, respectively. It can be seen from these photographs that all of the samples neck-in at the top and that miscellaneous holes and ruptures are randomly distributed throughout, being more predominant in some samples than in another. This phenomenon will also be explained in the discussion section. The x-ray diffraction patterns were made on clay samples both before and after irradiation. No difference was noted in these patterns which are shown in Appendix 4.

The reduced viscosity was determined for these samples as previously described and the results are presented in Tables 11, 12, 13, and 14, pages 56, 58, 60, and 62. The graphical results are given in Figures 29, 30, 31, and 32, pages 57, 59, 61, and 63. A summary of the results of the effects of $\overline{M}_v$ as a function of radiation time is given in Figure 33, page 64. The $\overline{M}_v$, rather unexpectedly, begins to decrease sometimes in less than 15 minutes irradiation time.

C. Irradiation of Monomer in the Presence of Miscellaneous Solids

The monomer was mixed in 1:1 weight ratio with varying particle sizes of silicon dioxide, aluminum oxide, zirconium-

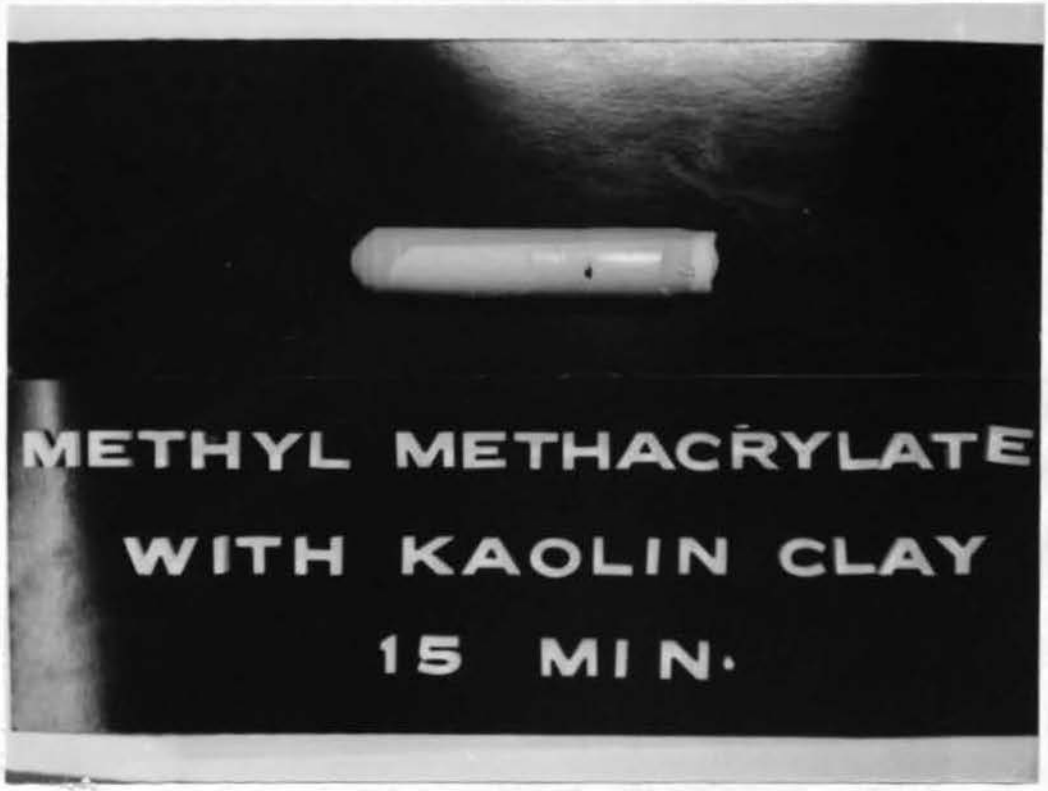


Figure 25. THE MONOMER-CLAY SAMPLE AFTER 15 MINUTES OF GAMMA RADIATION

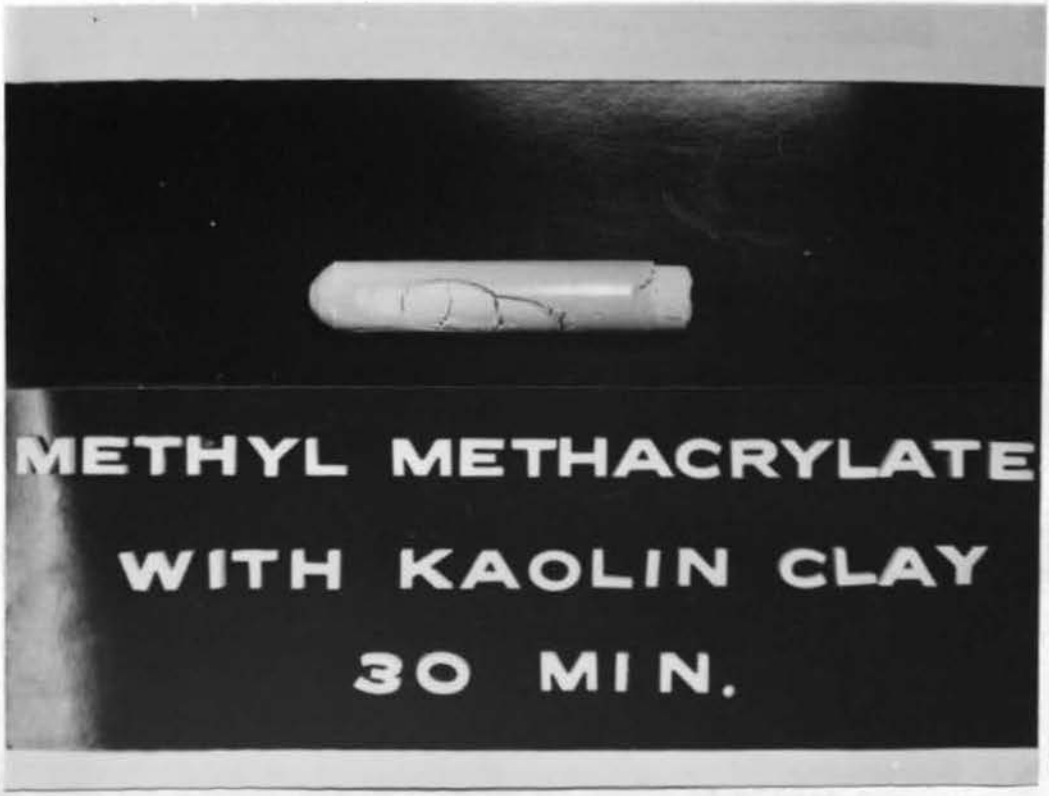


Figure 26. THE MONOMER-CLAY SAMPLE AFTER 30 MINUTES OF GAMMA RADIATION

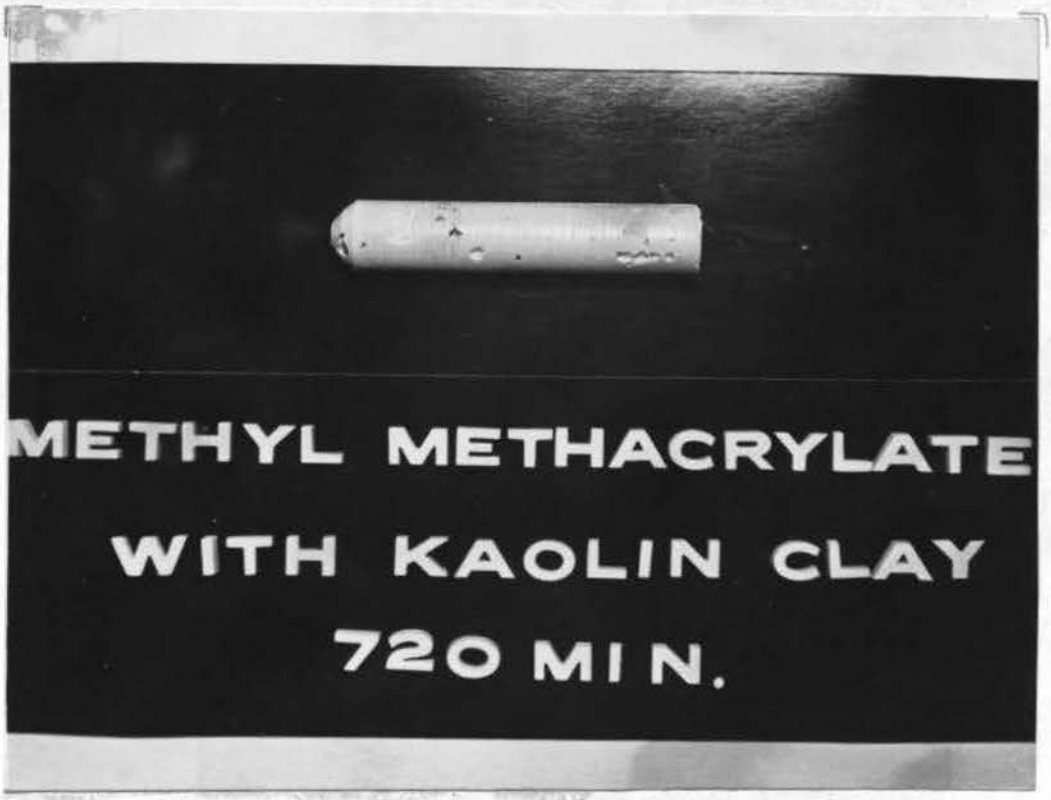


Figure 27. THE MONOMER-CLAY SAMPLE AFTER 720 MINUTES OF RADIATION

Figure 28. THE MONOMER-CLAY SAMPLE AFTER 1440 MINUTES OF RADIATION

TABLE 11. REDUCED VISCOSITY AS A FUNCTION OF CONCENTRATION FOR No. 17

Concentration (grams/100 ml)	Density (grams/ml^3) @ 30°C	Average Efflux Time (seconds)	Viscosity (centipoise) @ 30°C	Reduced Viscosity
0.5264	1.2457	202.4	2.0180	3.6506
0.2632	1.22606	128.2	1.2454	3.0510
0.1755	1.2202	109.6	1.0522	2.8430
0.1316	1.2171	101.4	0.9670	2.7293
0.1053	1.2151	97.1	0.9221	3.1822

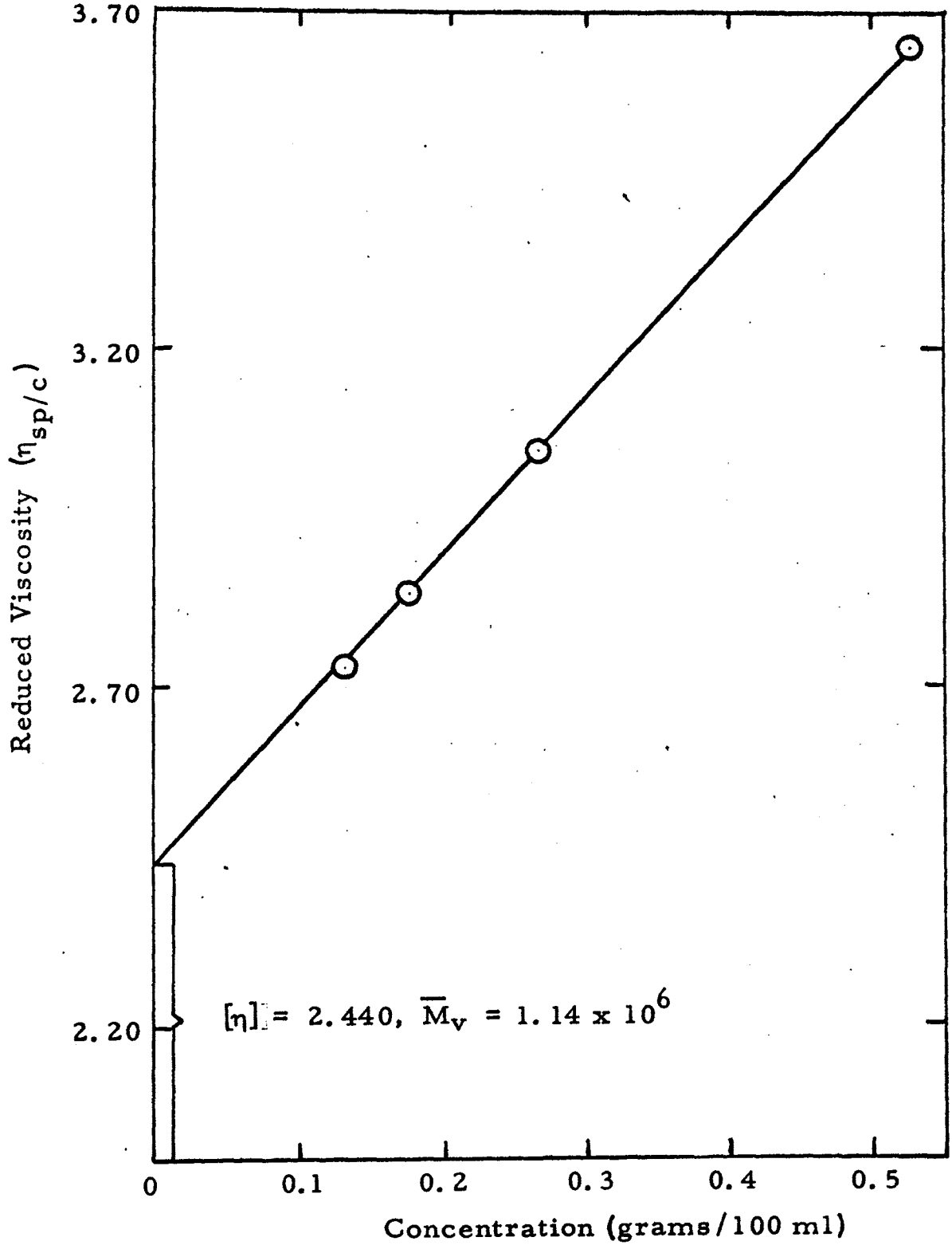


Figure 29. INTRINSIC VISCOSITY DETERMINATION OF SAMPLE No. 17

TABLE 12. REDUCED VISCOSITY AS A FUNCTION OF CONCENTRATION FOR No. 24

Concentration (gram/100 ml)	Density ($grams/ml^3$) @ 30°C	Average Efflux Time (seconds)	Viscosity (centipoise) @ 30°C	Reduced Viscosity
0.5134	1.2458	157.7	1.5043	2.2943
0.2567	1.2467	110.2	1.0638	2.1004
0.1711	1.2203	97.2	0.9270	1.9991
0.1284	1.2171	91.8	0.8699	2.0214
0.1027	1.2215	88.5	0.8351	2.0357

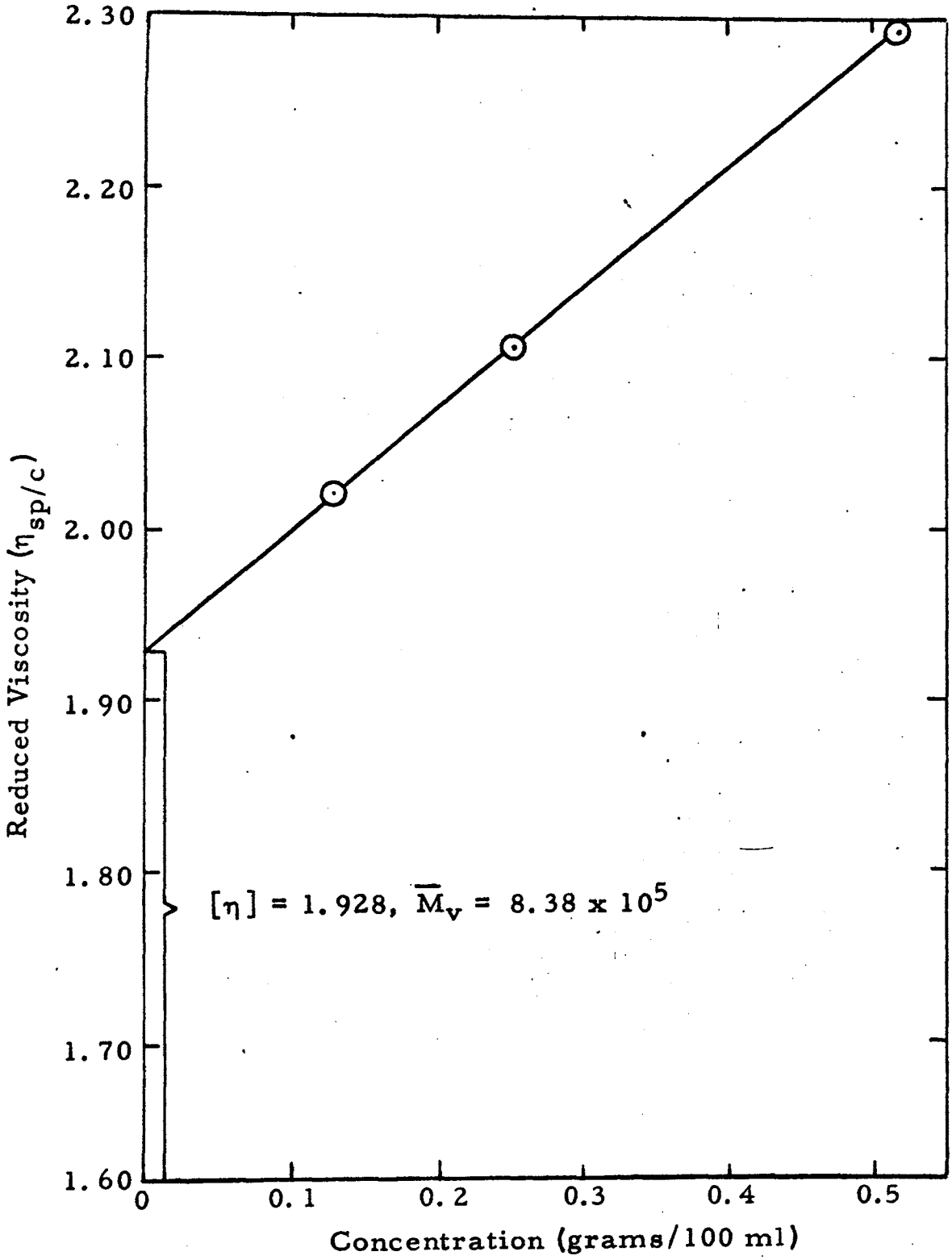


Figure 30. INTRINSIC VISCOSITY DETERMINATION OF SAMPLE No. 24

TABLE 13. REDUCED VISCOSITY AS A FUNCTION OF CONCENTRATION FOR No. 25

Concentration (grams/100 ml)	Density (grams/ml^3) @ 30°C	Average Efflux Time (seconds)	Viscosity (centipoise) @ 30°C	Reduced Viscosity
0.6770	1.2464	144.5	1.43166	1.5846
0.3385	1.2269	106.1	1.02251	1.4192
0.2257	1.2205	95.1	0.90583	1.3643
0.1693	1.2172	90.0	0.85172	1.3375
0.1354	1.2153	87.1	0.82092	1.3925

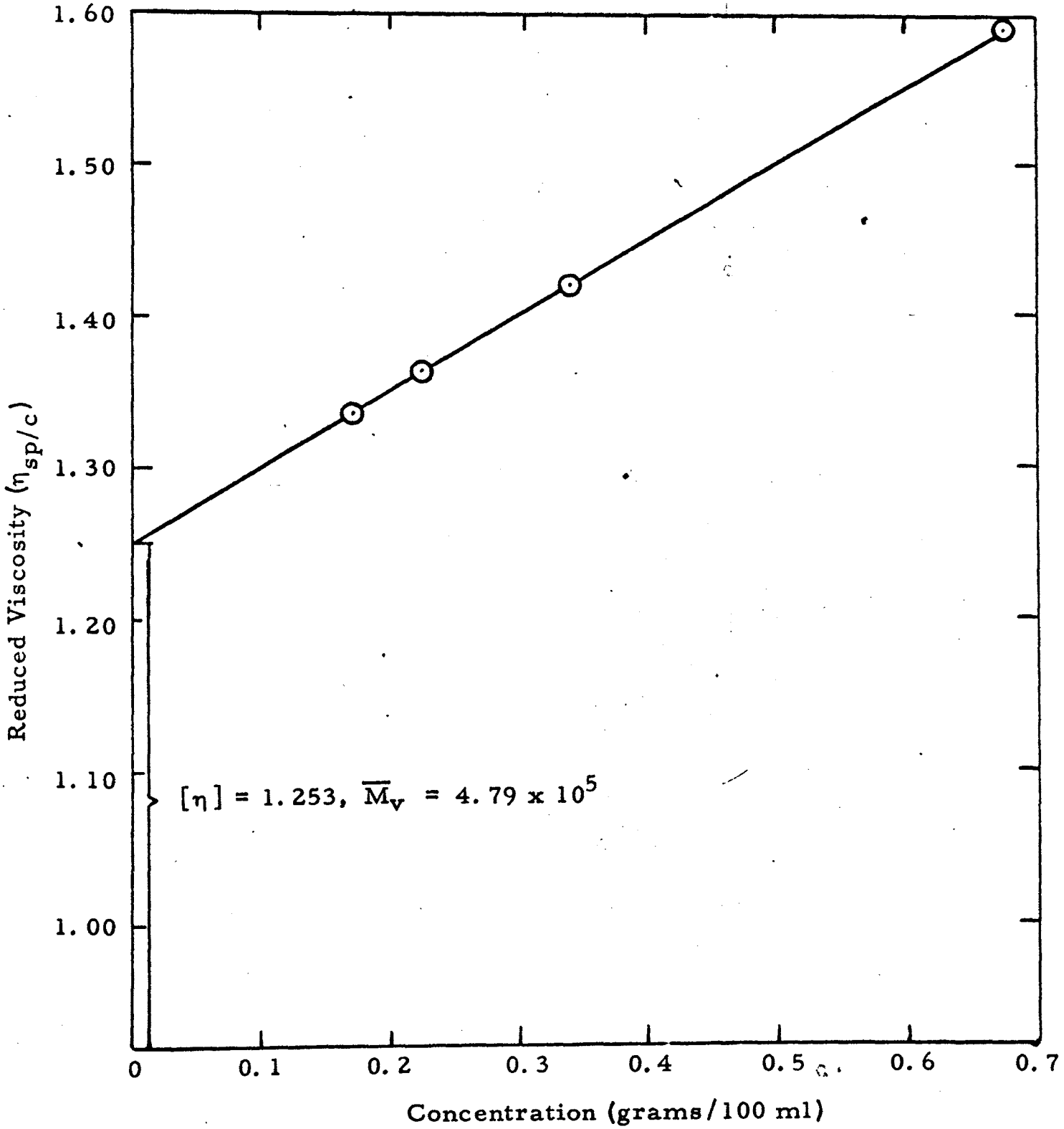


Figure 31. INTRINSIC VISCOSITY DETERMINATION OF SAMPLE No. 25

TABLE 14. REDUCED VISCOSITY AS A FUNCTION OF CONCENTRATION FOR No. 28

Concentration (gram/100 ml)	Density (grams/ml^3) @ 30°C	Average Efflux Time (seconds)	Viscosity (centipoise) @ 30°C	Reduced Viscosity
0.5876	1.2458	88.4	0.8551	0.4050
0.2938	1.2266	81.4	0.7699	0.3940
0.1959	1.2202	79.3	0.7444	0.3968
0.1469	1.2171	78.1	0.7301	0.3886
0.1175	1.2152	77.4	0.7218	0.3832

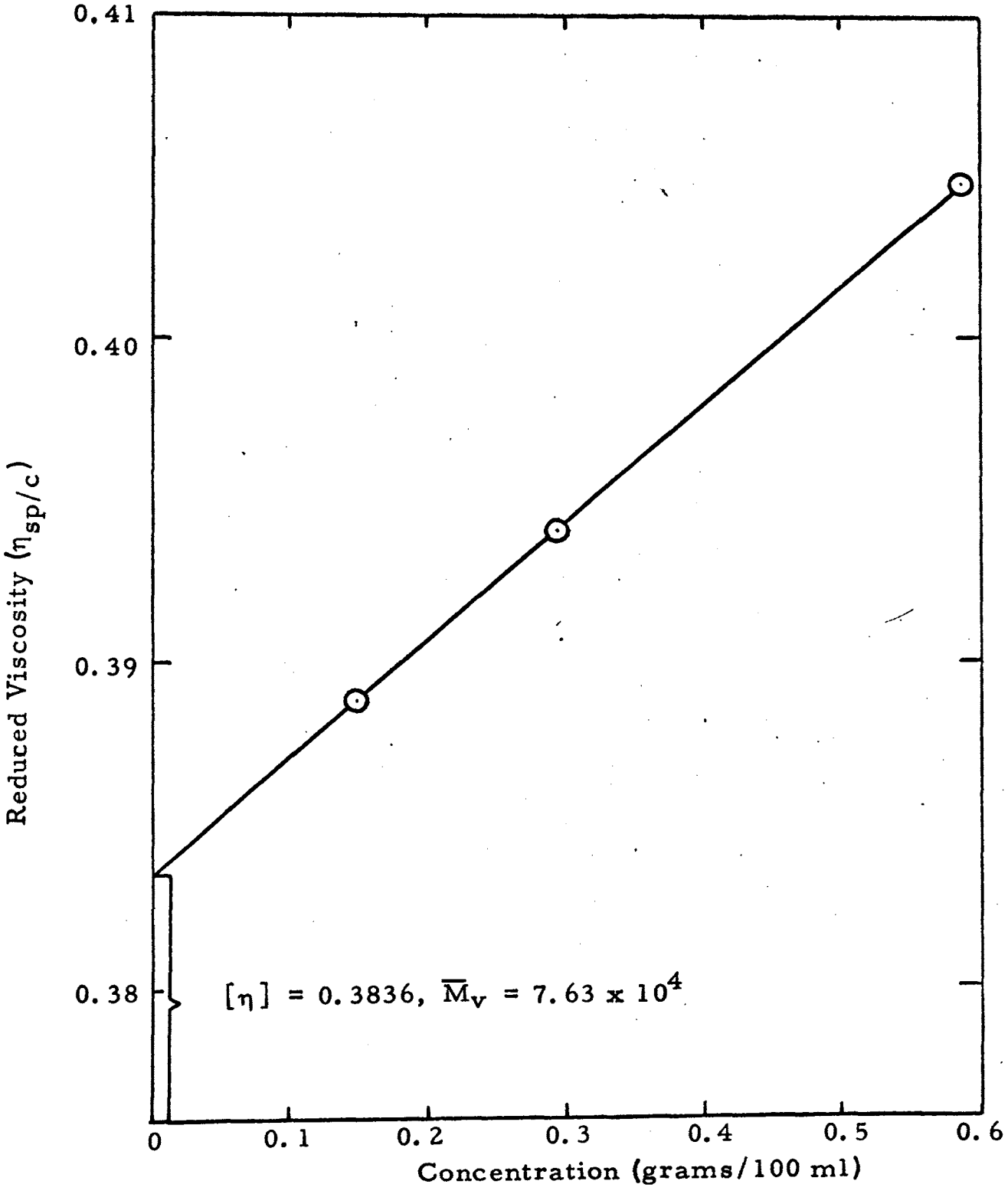


Figure 32. INTRINSIC VISCOSITY DETERMINATION OF SAMPLE No. 28

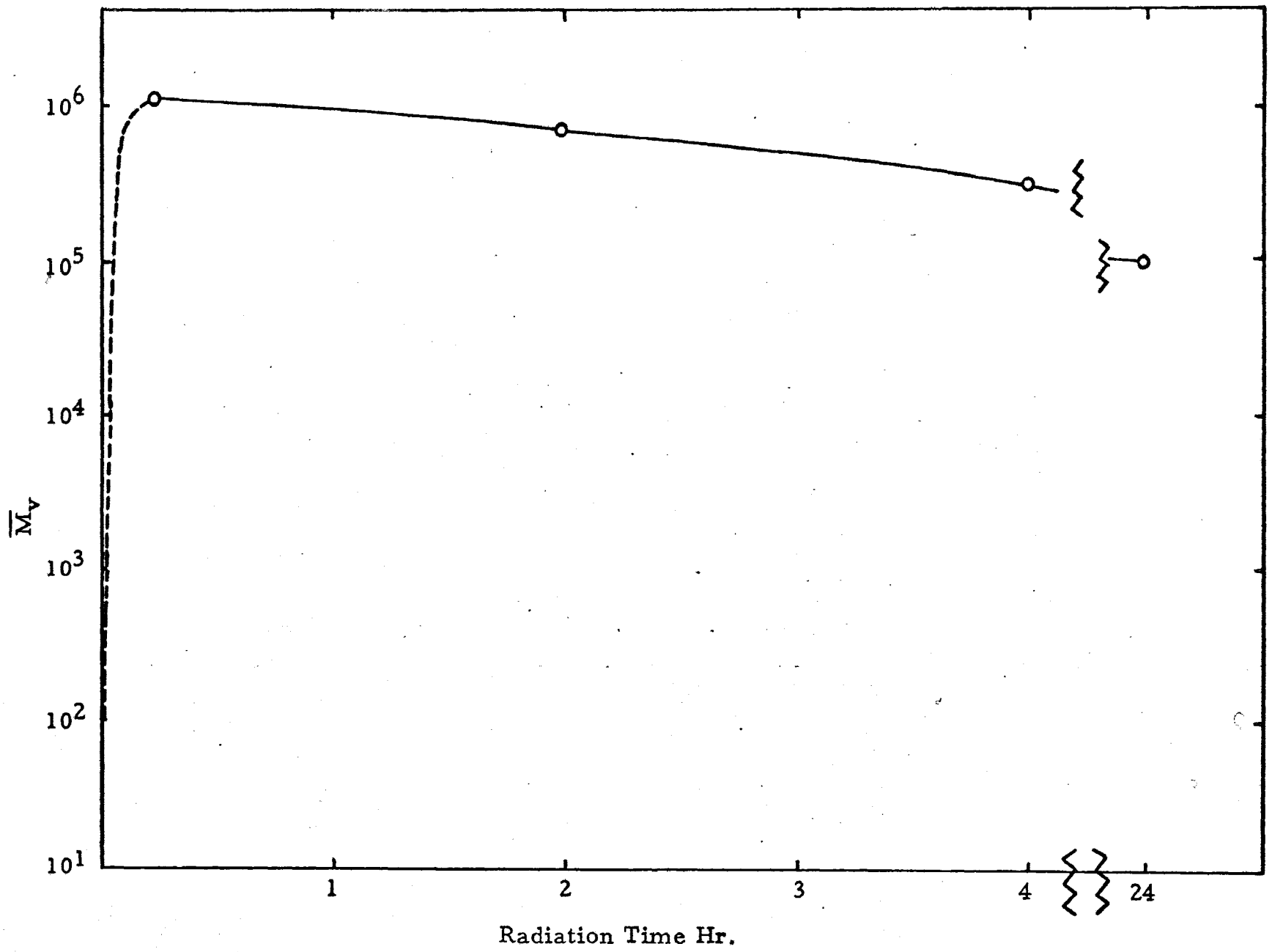


Figure 33. RADIATION TIME VS $\overline{M}_v$ FOR MMA-CLAY SAMPLES

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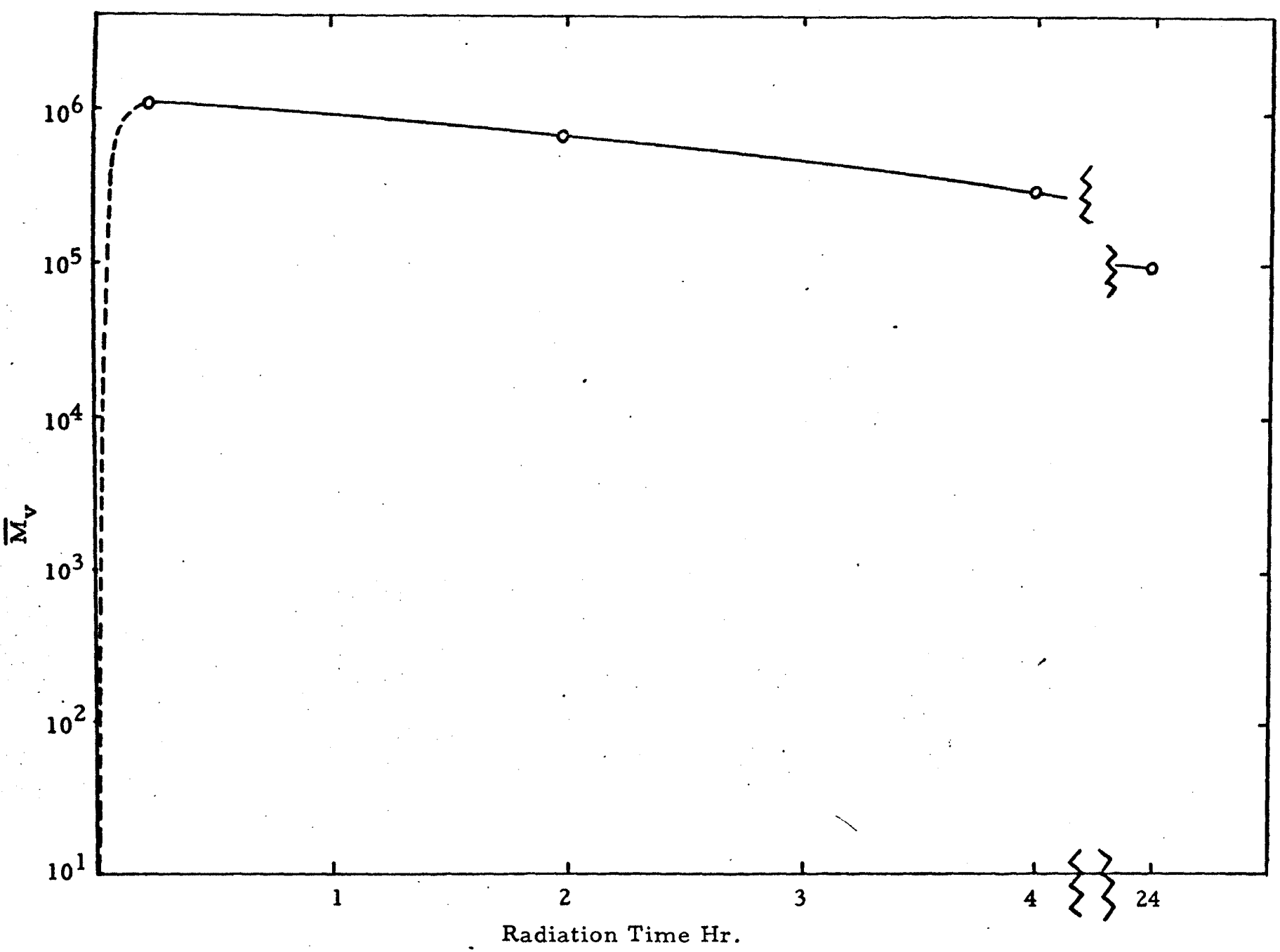


Figure 33. RADIATION TIME VS $\overline{M}_v$ FOR MMA-CLAY SAMPLES

silicon oxide and carbon. Details of these materials were given in Appendix 1. In addition to the above, a separate series of samples were run with monomer to clay weight ratio 20:1, 4:1, and 2:1. All of the above samples were prepared as previously described and irradiated for a period of 30 minutes. In only one case did any of these samples polymerize to a measurable extent in the 30 minutes irradiation period even though in most cases, the monomer was in intimate contact with the solid. The sample containing a 2:1 monomer clay ratio showed a definite viscosity increase but was far from being a solid. In fact, the remainder of the samples increased in viscosity much beyond that of the monomer alone irradiated for the same time period. The data accumulated on this phase of the work were not complete and will not be quantitatively reported in this thesis. However, these results suggested several interesting speculations which will be enumerated in the next section.

V. DISCUSSION OF RESULTS

It was noted that when the monomer was irradiated in the absence of clay or other solid materials that the bottom of the samples change in $\overline{M}_v$ at a faster rate than at the top. This phenomenon is attributed to the fact that the density of the polymer formed during the early stages of the reaction is greater than the monomer and therefore tends to settle to the bottom of the cell. This process occurs until the last monomer is polymerized to the gel state, at which point the motion of the polymer molecules are greatly restricted and further separation can not occur. It is further supposed that the bottom portion of the samples could begin to degrade before the top portion has completely polymerized. Figure 24, page 52, shows this change. If shorter or longer cells were used it would be expected that these curves would become closer together or that the differences would become more exaggerated.

It can be seen from the photographs of the unfilled polymer that cavities are at the surface and below the top position of the polymer. If the bottom of the sample began to decompose while the top position were still in the form of a gel any gaseous by-products evolved from the bottom would be trapped unless a large pressure gradient existed between the top and bottom of the sample.

There is no question that gaseous by-products are formed during the irradiation. When samples of the solid polymer were dissolved in solvents at room temperature an evolution of gases was evident. These gases were collected in an inverted test tube and ignited with a flame. They did support combustion as evidenced by a "Bark" when they were ignited. Another sample was heated gently to its softening point (about 110°C) and gas evolution was noted here. These gases were also combustible. The gases were not analyzed since the equipment was not available. However, hydrogen, carbon monoxide, methane, etc. would be expected to be decomposition products for this polymer. It is also not known if the gases are simply dissolved in the polymer or if they are held by other forces.

When the monomer was irradiated alone the maximum $\overline{M}_v$ occurred after four hours at the flux employed. It is assumed that the polymer has its optimum $\overline{M}_v$ at this point. A different flux or a different sample geometry may shift the position of the maximum $\overline{M}_v$. Further, it is assumed that the temperature of the polymer in the cell was the same as the temperature in the reaction pool since the reaction occurred at a slow enough rate that any heat generated could be readily dissipated.

Monomer samples in the presence of Ajax P clay run under

the same condition as for the monomer alone showed a very definite increase in the rate of reaction. After 15 minutes of irradiation time on the sample having a 1:1 weight monomer to clay ratio a solid product was obtained. After subsequent separation of the polymer from the clay it was found that the $\overline{M}_v$ of the polymer decreased continuously over the period from 15 minutes to 24 hours. This was somewhat surprising. The data indicate that a maximum $\overline{M}_v$ was obtained sometime before 15 minutes or that the rate of polymerization was increased by a factor of more than sixteen. Once more, these polymers were not adequately characterized since the necessary equipment was not available.

Photographs of the final monomer-clay mixture show that there is a definite necking in at the top of the sample as well as numerous cracks and voids. It is strongly believed that this may be due to temperature effects within the sample during irradiation that are associated with the increased reaction rate and the higher gamma absorption coefficient of the clay. The absorption coefficient varies roughly as the density and Z of the material. For the high energy gamma rays from the reactor, pair production is the predominant means of gamma interaction. The pair production coefficient varies directly with Z^2/A, or roughly with Z since Z/A is approximately constant for all materials.

There is little question that gaseous products form at an early stage of the reaction. Since the polymer molecules formed are not as mobile as they were in the absence of solid, density differences from top to bottom of the samples were not experienced and all of the polymer probably started to decompose at the same time. From the appearance of the sample it appears that the outer surface of the sample which was in contact with the aluminum cell walls remained cool while the inner portion may have been heated (due to the reaction and the gamma rays) and had expanded. This would account for the necking-in observed. If the polymer began to decompose while it was still in the state of a gel, and if there was a temperature rise in the polymer interior, the expanding gases could be expected to cause voids and cracks. The extent of the voids and cracks may be related to the gamma absorption, the temperature effects associated with the reaction and the geometry of the samples.

The addition of other solids such as silicon dioxide, zirconium silicon dioxide, aluminum oxide and carbon, to the monomer appeared to have little effect on the rate of polymerization. These observations may or may not be pertinent. The average particle size of the Ajax P clay was about two microns while the smallest particle size of the other solids was about 24 microns. Since the rate of polymerization may depend largely

on particle size (or the surface area to volume ratio) the tests performed here have no basis for comparison. A series of tests of various solids having the same particle sizes should be run with varying monomer to solid ratios. Only then could it be determined if particle size is a criterion or if the reaction rate is more dependent upon the density or chemical nature of the solids.

The previous results are based upon one value for the gamma flux. At present it is not known whether a higher or a lower molecular weight polymer would result from a higher or lower flux.

VI. CONCLUSIONS

An analysis of the data and results obtained in this study lead to the following conclusions:

1. When methyl methacrylate monomer is subjected to high energy gamma radiation a polymer is formed. The state of the final polymer is a function of irradiation time at a given flux; the polymer goes through phases of becoming a viscous liquid, a gel, a solid polymer of some maximum molecular weight and then the solid polymer begins to degrade with further irradiation. The criterion used for the extent of polymerization is the determination of the viscosity average molecular weight ($\overline{M}_V$). In addition to effecting the rate of polymerization the intensity of the gamma flux may also have an effect on the extent of polymerization and therefore the ultimate molecular weight.

2. After the polymer reaches the stage of gel, there are indications that portions of the polymer are degrading while the bulk of the polymer is still undergoing chain propagation. The molecular weight of the PMMA at the bottom of the samples increases faster and decomposes sooner than the material at the top of the samples. Density measurements made on various sections of the polymer as well as visual observations indicate that during the early stages of the reaction, the initial polymers

formed settle to the bottom of the aluminum cells because of the differences in densities between polymer and monomer. In some cases gaseous cavities were noted on the side surfaces of the solid samples. Further investigation revealed that there are gaseous by-products dissolved in the solid samples and that these gases are products of degradation, some of which are combustible. The equipment required was not available to analyze these gases, therefore a mechanism for breakdown was not postulated.

3. When the monomer is mixed with Ajax P Clay of average particle size of 2 microns in the weight ratio of 1:1 to form a stable paste, the rate of polymerization is greatly increased. A solid material is obtained in less than 15 minutes as compared to 240 minutes when the monomer is irradiated alone. The PMMA-clay samples show voids and cracks which are related to heat effects caused by either an exothermic reaction or gamma ray interaction with the clay, or possibly both. The extent of the temperature effects have not been pursued sufficiently to elaborate on the various possibilities in this thesis. Samples run with monomer to clay ratios of greater than 1:1 (where the clay could settle) resulted in only a slight increase in the rate of reaction.

4. When the monomer was irradiated in the presence of aluminum oxide, silicon dioxide, zirconium-silicon dioxide and

carbon, of particle sizes varying from about 24 microns to 1/8 inch lumps, no significant increase in reaction rate was noted. Since the smallest particle size of these materials was about 15 times greater than that of the clay no definite conclusions as to the effect of these species can be drawn. This investigation was of an exploratory nature and has raised more questions than it has answered. In particular, subsequent investigation into this area will have to consider the effects of: (1) the particle size (surface area to volumn ratios); (2) density of the mixture (i. e. the monomer-clay ratio); (3) higher heat absorption coefficient of the clay; (4) the dose rate; (5) the irradiation time, and (6) the chemical structure of the specimen to be irradiated.

VII. LIMITATIONS AND RECOMMENDATIONS

1. It has been observed that the PMMA formed by gamma irradiation has a difference in molecular weight between the top and bottom parts of the polymer. The polymer could not be characterized adequately due to equipment limitations. Therefore, fractionation is recommended in order to obtain an accurate molecular weight range.

2. Temperature was not measured during the irradiation. It would be better to measure the temperature particularly on samples containing clay. Sample heating by the radiation might be one of the determining factors on polymerization.

3. The polymer should be analyzed by mass spectrographic or chromatographic methods to determine the decomposition products.

4. The sample container used in this investigation was confined to a cylinder having a diameter of 3/4 inch and a height of 5 3/8 inches. However, the geometery and the height of the container should be varied in future work.

5. The radiation flux varied slightly from position D-1 and E-1. This variation did not appear to have any extra-ordinary effects on the result but it would be more consistent to run all

samples in the same position under the same radiation.

6. All runs were made at approximately the same radiation flux. It is suggested that data be taken at a lower dose rate such that the rate of polymerization and decomposition might be slower and easier to control. A better product with less holes and cracks might be expected, especially on the monomer-clay sample.

7. On samples run for periods longer than eight hours the total radiation time was made up of increments not exceeding eight hours. This situation could affect the final results, particularly with monomer-clay samples where temperature effect may be an important factor.

8. Different ratios of monomer to solid should be investigated thoroughly to determine the properties of the solids which influence the reaction rate. This study does not give enough information even to postulate whether the rate is primarily dependent of the chemical structure, surface area (particle size), density and some other properties of solids.

9. A better method of thoroughly mixing the monomer-clay sample would be favorable in order to get more uniform products.

10. Tests for mechanical properties have not been performed. It is suggested the tests of tensile strength, elongation and compression should be made in order to help characterize the final products.

11. Other vinyl compounds such as methyl acrylate or butyl-methacrylate should be used since the polymers of these monomers possess a marked degree of flexibility. Consequently products without holes and cracks can be expected.

BIBLIOGRAPHY

(1) Charlesby, A.: "Atomic Radiation and Polymers," pp. 52-54, Pergamon Press, New York, 1960.

(2) Bovey, F.A.: "The Effects of Ionizing Radiation on Natural and Synthetic High Polymers," p. 32, Inter-Science Publishers, Inc., New York, 1958.

(3) Ibid, p. 34.

(4) Ibid, p. 41.

(5) Ibid, p. 130.

(6) Ibid, p. 131.

(7) Ibid, p. 38.

(8) Ibid, p. 52.

(9) Lind, S.C.: "The Chemical Effects of α-Particles and Electrons," Chemical Catalog Co., New York, 1928.

(10) Eyring, H., J.O. Hirschfelder, and H.S. Taylor, J. Chem. Phys., 4, 479 (1936).

(11) Frank, J., and E. Rabinowitch, Trans. Faraday Soc. 70, 120 (1934).

(12) Lind, S.C., D.C. Bardwell, and J.H. Perry, J., Am. Chem. Soc., 48, 1556 (1926).

(13) Hayward, J.C., Jr., "Polymerization of Ethylene Initiated by Gamma Radiation," (Thesis), Department of Chemical Engineering, Yale University, 1955.

(14) Lind, S.C., Chairman, "Symposium on Radiation Chemistry and Photochemistry," University of Notre Dame, 1947; J. Phys. Colloid. Chem. 52, No. 3 (1948).

(15) Lind, S.C., J. Phys. Colloid. Chem. 52, 437 (1948).

(16) Burton, M., "Annual Review of Physical Chemistry," Vol. I (Radiation Chemistry, p. 113), Annual Reviews Inc., Stanford (California), 1950.

(17) Seitzer, W.H., R.H. Goeckermann, and A.V. Tobolsky, J. Am. Chem. Soc., 75, 755 (1953).

(18) Charlesby, A., Nature, 171, 167 (1953).

(19) Lawton, E.J., A.M. Bueche, and J.S. Balwit, Nature, 172, 76 (1953).

(20) Miller, A.A., E.J. Lawton, and J.S. Balwit, J. Polymer Sci., 14, 503 (1954).

(21) Inokuti, M., and M. Dole, J. Polymer Sci., Part 1, Vol. 1, p. 3289 (1963).

(22) Wall, L.A., J. Polymer Sci., 17, 141 (1955).

(23) Roberts, D.E., J. Research Natl. Bur. of Standards, 44, 221 (1950).

(24) Simha, R., Trans. N.Y. Acad. Sci., 14, 151 (1952).

(25) Alexander, P., A. Charlesby, and M. Ross, Proc. Roy. Soc. (London), A223, 392 (1954).

(26) Wall, L.A., and D.W. Brown, J. Res. Natl. Bur. of Standards, 57, 131 (1956).

(27) Shultz, A.R., P.I. Roth, and G.B. Rathmann, J. Polymer Sci., 27, 495 (1956).

(28) Price, W.J., "Nuclear Radiation Detective," 2nd ed., McGraw Hill, New York, 1964.

(29) Billmeyer, F.W., "Textbook of Polymer Science," p. 80, Interscience Publishers, New York, 1962.

VITA

The author was born in Fukien, China, on December 4, 1939.

He joined Taiwan Christian College in 1957 where he obtained his Bachelor's degree in Chemical Engineering in 1961. He served as second lieutenant in the Military Police Corps of Chinese Army for one and a half years. From October 1962 to May 1963, he was employed by the Chinese Government as an inspector of industry.

In September 1963, he entered the University of Missouri at Rolla as a graduate student in Chemical Engineering to pursue the Master of Science degree.

APPENDICES

APPENDIX 1. MATERIALS

Methyl Methacrylate Monomer: Liquid, analyzed reagent, meets A. C. S. specifications; viscosity, 0.57 cps @ 25°C; density 0.939 @ 25°C/15.6°C; 50 ppm monomethyl ether of hydroquinone is used as inhibitor; Matheson, Coleman and Bell Company, Norwood, Ohio. Used as subject of investigation.

Ajax P Clay: Powder of fine controlled particle size (2 microns) with chemical analysis data; silicon dioxide 45.20%, aluminum dioxide 38.08%, iron oxide 0.49%, titanium dioxide 1.52%, calcium oxide 0.26%, magnesium oxide 0.30%, sodium oxide 0.02%, potassium oxide 0.04%, loss on ignition 13.51%. Georgia Kaolin Company, Elizabeth, New Jersey. Used as the filler of investigation.

Sample Cells: Aluminum tubes of given dimensions (3/4" I.D. x 5-3/8" length) with caps, Corral, Wodiska y Ca., Tampa, Florida. Used as the sample container.

Ferrous Sulfate ($FeSO_4 \cdot 7H_2O$): Granular, analyzed reagent meets A. C. S. specifications, J. T. Baker Chemical Company, Phillipsburg, N. J. Used to prepare the Fricke dosimeter solutions.

Sulfuric Acid: Reagent, meets A. C. S. specifications, assay 95.5-96.5% H_2SO_4, General Chemical Division, Allied Chemical

Company, New York, N. Y. Used to prepare the Fricke dosimeter solutions.

Miscellaneous Solids: Aluminum oxide 325 mesh, tabular alumina, ZrO_2 - SiO_2 600 mesh, zirconium sand, zirconium silicate, silica 390 mesh, silica sand, activated carbon and graphite obtained from the Department of Ceramics, UMR. Used as fillers in investigation.

APPENDIX 2. APPARATUS

Balance: Analytical, model 640D, property of the Paint and Polymer Chemistry Laboratory, UMR, 0-100 grams, Voland and Sons Inc. New Rochelle, N. Y. Used to make weight determinations to 0.0001 gram.

Viscometers: Both Cannon-Ubbelohde No. $\frac{75}{D440}$ and Cannon-Fenske-Ostawald No. $\frac{200}{D151}$ types of viscometers, manufactured by the Cannon Instrument Co., State College, Pa., used to make the viscosity measurements.

Constant Temperature Bath:

1. Water Bath, KIMAX
2. Bronwill Contact-Thermometer, Catalog No. 7937, H-B Instrument Co., used to control the constant temperature at 30°C.
3. Stirrer, MSM No. 27278, catalog No. S-7 1590, Sargent & Co. Used to agitate the water.
4. Variac, Type 500B, Standard Electrical Product Co., Dayton, Ohio. Used to adjust the voltage.

Stop Watch: Swiss made, 0.2 second, UMR Chemistry Laboratory. Used to measure the efflux time.

Vacuum Pump: MSM P1 24131, Catalog No. 91105, Central Scientific Co., Chicago, Ill. Used to remove the traces of solvent for cleaning the viscometers.

Glassware: An assortment of standard laboratory glassware, obtained from the Chemical Engineering Department Stockrooms, is used.

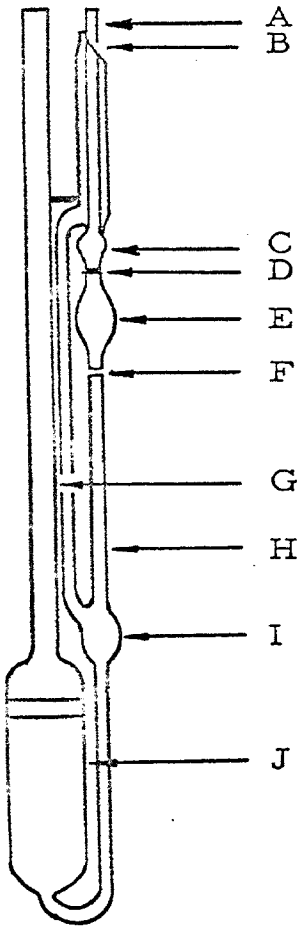
APPENDIX 3

VISCOSITY DETERMINATIONS

1. Prodecure for the Use of the Cannon-Ubbelohde Dilution Viscometer.

2. Computer Program for the Calculation of the Experimental Results.

PROCEDURE FOR THE USE OF THE CANNON-UBBELOHDE DILUTION VISCOMETER



Cannon-Ubbelohde Viscometer

1. Clean the viscometer with acetone and dry with a vacuum pump. Periodically, traces of organic deposits should be removed with cleaning solution.

2. If there is a possibility of dust or other solid material in the liquid sample, the sample should be filtered through a cintered glass filter.

3. Charge a measured volume of sample (8.0 to 10.0 ml) directly from the pipette through tube G into the lower reservoir of the viscometer.

4. Place the viscometer into the holder and insert it into the constant temperature water bath (@ 30°C). Vertically align the viscometer in the bath.

5. Allow approximately 20 minutes for the sample to come to the bath temperature.

6. Place a finger over tube B and apply suction to tube A until the liquid reaches the center of bulb C. Remove finger from tube B, and immediately place it over tube A until the sample drops away from the lower end of the capillary into bulb I. Then remove finger and measure the efflux time.

7. To measure the efflux time, allow the liquid sample to flow freely down past etch mark D, measuring the time for the meniscus to pass from the etch mark D to etch mark F to the nearest 0.1 second.

8. Without recharging the viscometer, make check determination by repeating steps 6 and 7 until the efflux times are nearly the same. (approximately 0.1 second difference).

9. Dilute sample by adding a measured quantity of solvent from pipette directly into the lower reservoir of the viscometer. Mix the original sample and the solvent by applying slight pressure to tube B several times, and shake the viscometer.

10. Repeat steps 5 to 8. Additional dilution may be made if necessary.

COMPUTER PROGRAM FOR THE CALCULATION OF THE EXPERIMENTAL RESULTS

The following is a Fortran 2 computer program, in which C stands for concentration, R stands for density, T stands for efflux time, V for viscosity, and VRED for reduced viscosity. The definition of reduced viscosity is shown in Table 15, page 90.

```
C       DATA EVALUATION OF EXPERIMENTAL RESULTS
        DIMENSION C(5), R(5), T(5), V(5), VRED(5)
        DO 1000 III=1, 16
        READ 1, C(1), R1, R2
      1 FORMAT (3F8.5)
        READ 4, (T(I), I=1, 5)
      4 FORMAT(5F10.1)
        R(1)=R1
        DO 2 I=2, 5
        TK=I
        TW=I-1
        C(I)=C(1)/TK
      2 R(I)=(R1+TW*R2)/TK
        VZ=R2*(0.00806*74.8-2.30981/74.8)
        PRINT 100
        PRINT 102
        DO 5 I=1, 5
        V(I)=R(I)*(0.00806*T(I)-2.30981/T(I))
        VRED(I)=(V(I)/VZ-1.0)/C(I)
      5 PRINT 101, I, C(I), R(I), T(I), V(I), VRED(I)
    100 FORMAT(//7X1HI, 2X13HCONCENTRATION, 2X7HDENSITY,
       13X11HEFFLUX TIME, 2X9HVISCOSITY, 2X7HREDUCED)
    102 FORMAT(59X9HVISCOSITY//)
    101 FORMAT(6XI2, 4XF8.5, 5XF8.5, 4XF8.1, 4XF8.5, 3XF8.5)
   1000 CONTINUE
        STOP
        END
```

TABLE 15. NOMENCLATURE OF SOLUTION VISCOSITY[29]

Common Name	Recommended Name	Symbols and Defining Equations
Relative viscosity	Viscosity ratio	$\eta_r = \eta/\eta_o = t/t_o$
Specific viscosity		$\eta_{sp} = \eta_r - 1 = (\eta - \eta_o)/\eta_o = (t - t_o)/t.$
Reduced viscosity	Viscosity number	$\eta_{red} = \eta_{sp}/c$
Inherent viscosity	Logarithmic viscosity number	$\eta_{inh} = \ln\eta_r/c$
Intrinsic viscosity	Limiting viscosity number	$[\eta] = (\eta_{sp/c})_{c \to o} = [(\ln \eta_r)/c]_{c \to o}$

APPENDIX 4

X-RAY DIFFRACTION PATTERNS OF AJAX P CLAY

X-ray diffraction patterns were made on the clay before and after 8 hours of irradiation. Figure 34 and Figure 35, pages 92 and 93 showed that there was not any change in the composition of clay.

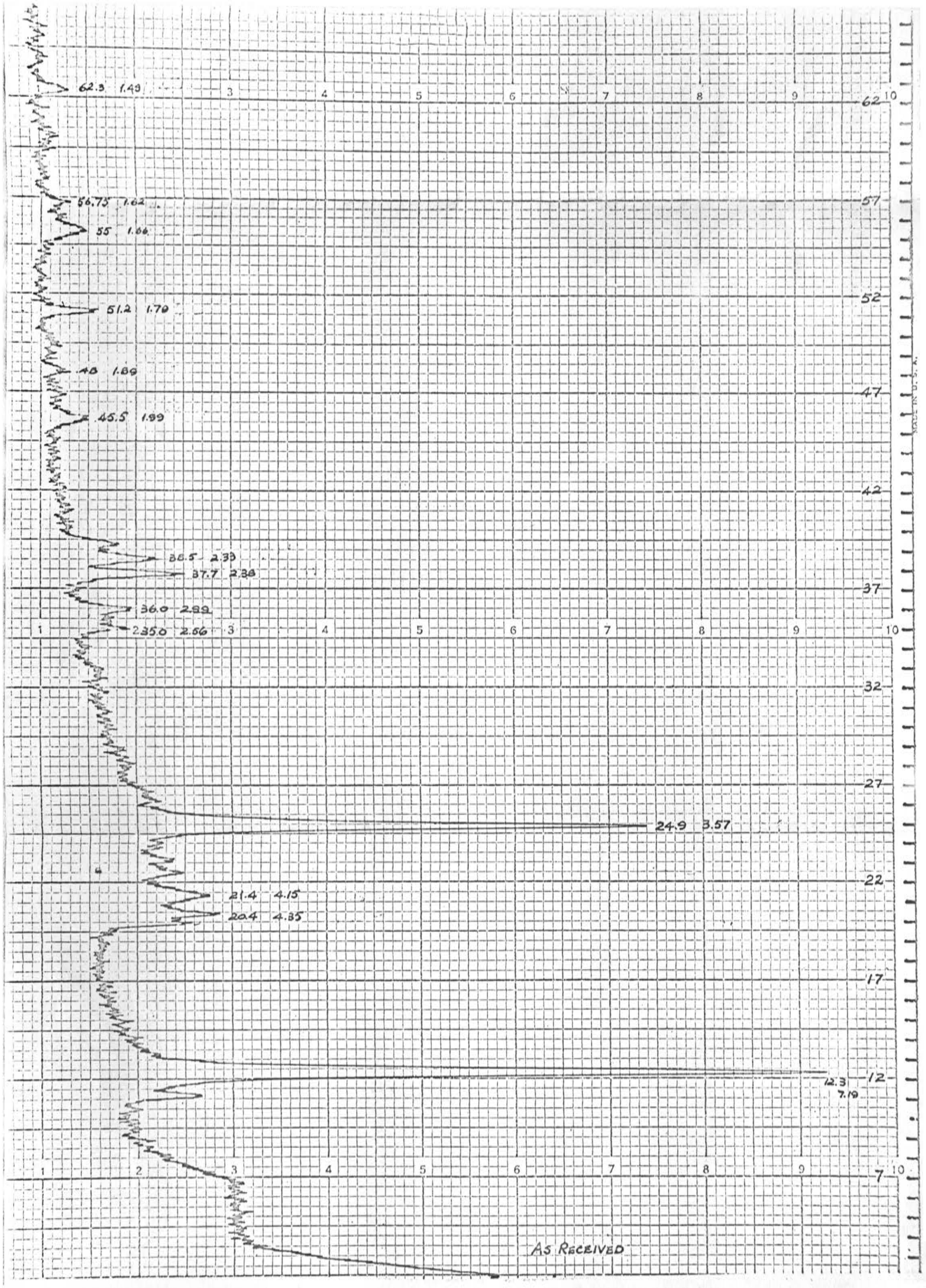


Figure 34. X-RAY DIFFRACTION PATTERN OF AJAX P CLAY AS RECEIVED

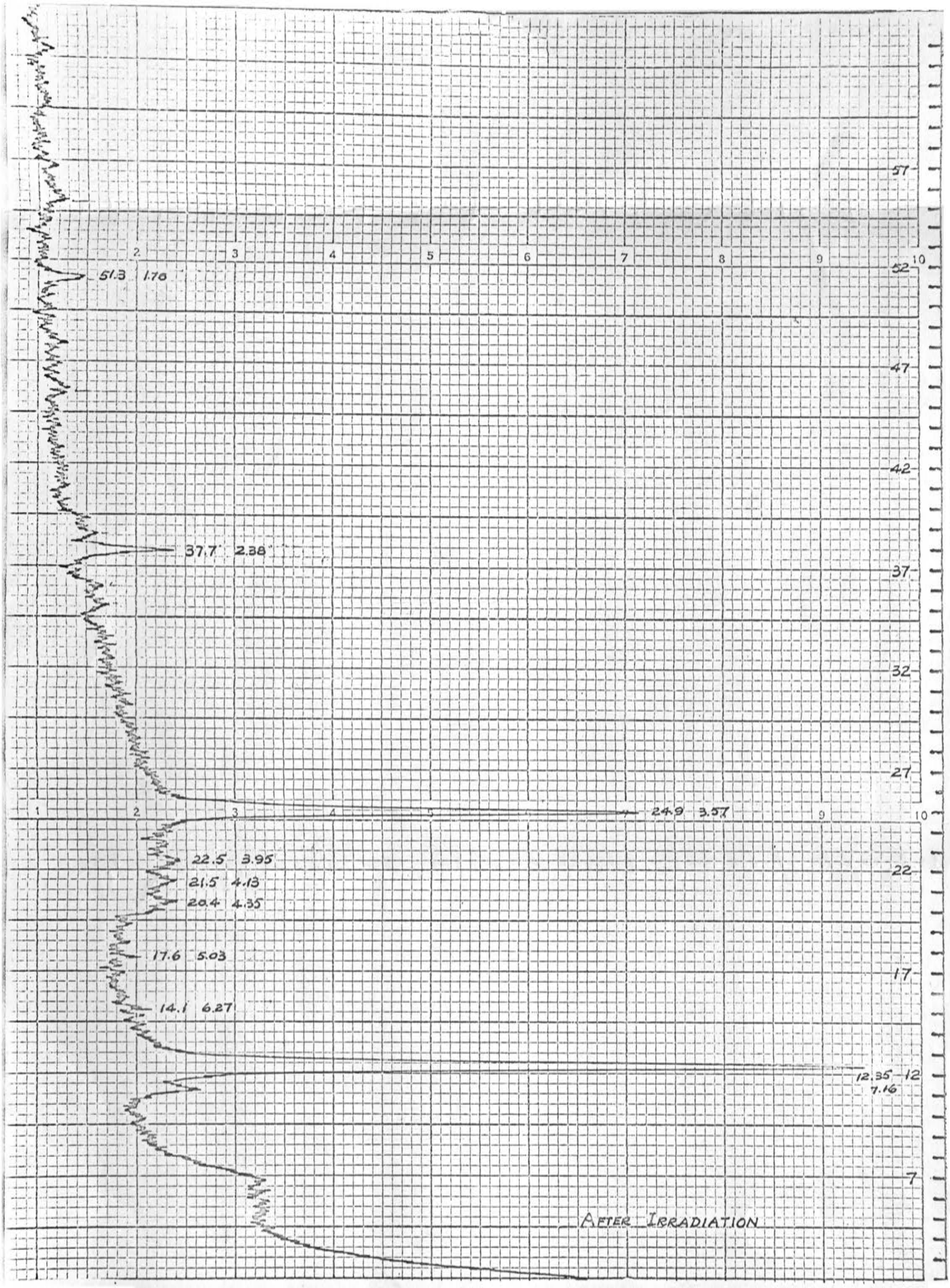


Figure 35. X-RAY DIFFRACTION PATTERN OF AJAX P CLAY AFTER IRRADIATION